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Construction and progress of small molecule-based coupled electrolyzers

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Abstract

Coupled electrolyzer is a desirable way to realize efficient energy conversion from electricity to chemical energy. Using coupled electrolyzers highly valuable chemicals (e.g., H₂, CH_xCOO⁻, nitrile, S, NH₃, CO) can be obtained at low voltages, environmental pollutants can be alleviated, and wastewater (e.g., ammonia, urea, hydrazine) can be recycled. They are even helpful to realize the goal of carbon peaking and carbon neutrality. Compared to traditional chemical methods, small molecule-based coupled electrolyzers are more cost-efficient. This review summarizes state-of-art of coupled electrolyzers, mainly the replacement of oxygen reduction reaction (OER) with oxidation reactions of small molecules and their further coupling with cathodic reduction reactions such as hydrogen evolution reaction (HER), oxygen reduction reaction (ORR), CO₂ reduction reaction (CO₂RR), N₂ reduction reaction (NRR) and other reduction reactions of matching small molecules. In terms of oxidation reactions of small molecules, two types of reactions are covered: sacrificial agent oxidation reaction (SAORs) and electrochemical synthesis reaction (ESRs). After detailing the design principle of coupled electrolyzers and several oxidation reactions of small molecules, construction, characterization and performance of coupled electrolyzers are systematically overviewed along with discussion and outline of current challenges and prospects of this appealing strategy.

Keywords: Coupled electrolyzer; Oxidation reactions of small molecule; Cathodic reduction reactions

1. Introduction

Excessive fossil fuels consumption has led to increasing environmental pollution and energy depletion. Seeking sustainable and clean energy alternative to fossil is thus highly imperative. There are different kinds of newly appeared energies such as solar, windy, tidal energy. Unfortunately, they cannot be directly integrated into modern industrial systems before being transformed to electricity.^[1] In order to maximize the utilization efficiencies of these energies with low costs, novel energy conversion systems are highly required. Among different developed strategies, electrochemical energy conversion scenario have been attracted extensive attentions because they storage these intermittent energies with high efficiencies, and meanwhile obtain high valuable chemical products, in some cases even remove environmental pollutants.^[2-3]

An electrochemical energy conversion system is generally composed of an anodic electrooxidation reaction and a cathodic electroreduction reaction in aquatic environment. In most case, an anodic reaction refers to oxidation of small molecules, among which oxygen evolution reaction (OER) is the most known reaction in that most systems are built in aqueous solutions. However, OER proceeds a four-electrons transfer process and has sluggish kinetic, thus always suffering from higher overpotentials in different cases. In other words, water splitting into hydrogen is heavily limited by high energy consumption required for OER to produce low valuable O_2 .^[4-7]

To tackle such a problem, the replacement of OER with oxidation reactions of small molecules on the anode (**Figure 1a**) has attracted much attentions in recent years in that these oxidation reactions just need lower oxidation potentials and meanwhile the obtained oxidation products can be highly valuable.^[8] According the summary of some theoretical oxidation potentials of a series of small molecules in KOH media (**Table 1**), oxidation reactions of such small molecules can be divided into two types (**Figure 1b, 1c**): sacrificial agent oxidation reactions (SAORs) and electrochemical synthesis reactions (ESRs). The molecules involved in SAORs includes ammonia, urea and hydrazine. Since these molecules are poisonous and generally regarded as main pollutants in wastewater, their removal *via* SAORs plays an important role in recycling wastewater. In the meantime, the molecules used for ESRs cover alcohol, aldehyde, glucose, amine and S². Different from environmental pollutants, oxidation of these molecules produces high value-added chemicals (e.g., CH_xCOO⁻, glucaric acid, benzonitrile and S), which might be more cost-effective routes than traditional chemical methods.



Figure 1. (a) polarization curves of HER, SAORs/ESRs, OER and ORR. (b-c) Schematic diagram of coupled electrolyzers.

As for electroreduction reactions occurring on the cathode, they mainly contain hydrogen evolution reaction (HER), oxygen reduction reaction (ORR), CO₂ reduction reaction (CO₂RR), N₂ reduction reaction (NRR), and reduction reactions of other small molecules. For example, HER is highly desirable for hydrogen production. As one of the most promising carriers for renewable energy, hydrogen is eco-friendly, has plentiful resources and more importantly possesses a high energy density.^[9] In this context, hydrogen has been produced by use of some traditional technologies, such as water gas, natural gas reforming and methanol steam reforming. Compared to them, H_2 production via HER is the most cost-effective and environment friendly strategy where energy consumption is low and no carbon emission happens.^[10] Meanwhile, the combination of ORR with anodic oxidation reactions of small molecules can be used to assemble fuel cells (Figure 1c). High energy output is expected based on high reaction potentials of such systems.^[11-12] Another example is CO₂RR. In recent years, extensive efforts have been made to CO₂RR. This is partially because it probably helps to reduce greenhouse effect from CO₂, eventually satisfying the goal of carbon peaking and carbon neutrality; partially because it offer an economical way to generate valuable chemical products.^[13-14] The recently booming NRR is assumed to be a promising strategy to convert abundant N₂ to valuable NH₃ under mild conditions, avoiding traditional coal gasification at high economic and environmental cost.^[15] NO₃

reduction reaction (NO₃⁻RR) is also an emerging electrochemical strategy for generating value-added chemicals from pollutant NO₃^{-,[16]} Nitro compounds (R-NO₂) was reduced to amino compounds (R-NH₂) when water was directly applied as hydrogen source.^[17] Recently, reduction of biomass-derived aldehydes such as 5-HMF for producing biodiesel exhibits a cost-effective approach, achieving the upgrade of renewable and cheap small molecules.^[18]

The integration of as-mentioned cathodic reactions (e.g., HER, ORR, CO₂RR, NRR and others) with anodic ones (e.g., SAORs, ESRs) then steps on the stage. Such an interesting and profitable combination is so-called as coupled electrolyzers (Figure 2), which can be further driven by renewable energy (e.g., hydrogen, wind, solar energy). In other words, more efficient production of highly value-added chemicals (e.g., NH₃, CH_xCOO⁻, nitrile, etc.) that are extremely important for fertilizer, plastic, chemical and medicine applications will be realized. Meanwhile, pollution problems of ammonia, urea and hydrazine in wastewater are possibly to be resolved. Moreover, coupled electrolyzers can directly generate electricity via constructing fuel cells based on applied redox reactions. For example, direct methanol fuel cells (DMFCs) have been assembled through coupling ORR with methanol oxidation reaction, offering high safety and energy density. Namely, this strategy addressed the issues of fossil energy shortage and environmental pollution caused by petrol vehicle.^[19] In this context, coupled electrolyzers based on small molecule redox reactions have exhibited promising prospect. However, relevant hybrid devices are still in infancy in that the pathways, where most reports only overviewed the small molecules oxidation reactions as replaced OER to assist hydrogen production. Meanwhile the reasonable classification of such systems have not been universally acknowledged yet, since reaction mechanisms behind are hard to well defined.[20-22]

In this review, we aim at offering a full image on state-of-art coupled electrolyzers. It firstly summarizes the conception and classification strategies for coupled based on small molecule oxidation and reduction reactions, including the introduction of small molecule redox reactions, catalyst design with aid of the structure-activity relationship, and construction principle and configuration of coupled electrolyzers. Then the classification and recent progress of typical small molecule reactions, such as the characterization of catalysts, catalytic mechanism and product analysis measured by advanced tools (e.g., in situ, operando techniques), are provided. Subsequently, the effective construction of various coupled electrolyzers in

terms of conserving energy and generating value-added compounds/contamination remediation are overviewed. Finally, a summary of current challenges and research orientations are outlined for the future designing of efficient coupled electrolyzers. **Table 1**. Theoretical potential of small molecule oxidation and reduction reactions.

			Theoretical
	Substrate	Half-reactions	potential
			(V vs. RHE)
	H ₂ O	$4OH^{-} \rightarrow 2H_2O + O_2 + 4e^{-}$	0.40 ^[23]
	Ammonia	$2NH_3 + 6OH^2 \rightarrow N_2 + 6H_2O + 6e^2$	-0.77 ^[24]
	Urea	$\mathrm{CO}(\mathrm{NH}_2)_2 + 6\mathrm{OH}^2 \rightarrow \mathrm{CO}_2 + \mathrm{N}_2 + 5\mathrm{H}_2\mathrm{O} + 6\mathrm{e}^2$	-0.46 ^[25]
	Hydrazine	$N_2H_4 + 4OH^2 \rightarrow N_2 + 4H_2O + 4e^2$	-0.33 ^[26]
Anodic	Methanol	$CH_3OH + 5OH^- \rightarrow HCOO^- + 4H_2O + 4e^-$	0.103[27]
oxidation	Ethanol	$CH_3CH_2OH + 5OH^2 \rightarrow CH_3COO^2 + 4H_2O + 4e^2$	-0.72[28]
reaction	Glycerol	$C_3H_8O_3 + 8OH^- \rightarrow 3HCOOH + 5H_2O + 8e^-$	-0.69 ^[29]
	Benzyl alcohol	$Ph-CH_2OH + 4OH \rightarrow Ph-COOH + 3H_2O + 4e^{-1}$	-0.35[30]
	HMF	$HMF + 6OH^{-} \rightarrow FDCA + 4H_{2}O + 6e^{-}$	-0.53 ^[31]
	Formaldehyde	$2\text{HCHO} + 4\text{OH}^{-} \rightarrow 2\text{HCOO}^{-} + \text{H}_2 + 2\text{H}_2\text{O} + 2\text{e}^{-}$	-0.22 V
	Glucose	$C_{12}H_{12}O_6 + 6OH^- \rightarrow C_{12}H_{10}O_8 + 6e^-$	-0.78 ^[32]
	Amine	$Ph-CH_2NH_2 + 4OH \rightarrow Ph-CN + 4H_2O + 4e$	-0.77 ^[33-34]
	Sulfion	$S^{2-} \rightarrow S + 2e^{-}$	-0.48 ^[35]
	H ₂ O	$4H_2O+4e^- \rightarrow 2H_2 + 4OH^-$	-0.83
Cathodic	O ₂	$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$	0.40
reduction	CO ₂	$\rm CO_2 + 2H^+ + 2e^- \rightarrow \rm HCOOH_{(aq)}$	-0.12[36]
reaction	CO ₂	$\rm CO_2 + 2H^+ + 2e^- \rightarrow \rm CO_{(g)} + H_2O$	-0.10 ^[36]
	N ₂	$N_2 + 6H^{\scriptscriptstyle +} + 6e^{\scriptscriptstyle -} \rightarrow 2NH_{\rm 3(aq)}$	0.092[37]
	NO ₃ -	$NO_3 - + 6H_2O + 8e^- \rightarrow NH_3 + 9OH^-$	0.69 ^[38]



Figure 2. Schematic diagram of sustainable energy based on coupled electrolyzers

2. Design principles

2.1 Oxidation reactions of small molecules

Oxidation reactions of small molecules taking place at the anode in the coupled electrolyzer systems play an important role in determining the device efficiencies. In order to improve practical value, the basic principle is to choose small molecules that are widely available and cheap, such as those derived from easily generated or abundant reservation in nature. Meanwhile, they must be highly soluble in water at room temperature. Furthermore, their theoretical potentials need to be low enough in comparison with that of OER (**Table 1**). In these regards, several small molecules have been employed up to date, including ammonia, urea, hydrazine (N_2H_4), alcohol, aldehyde, glucose, amine, and sulfion.

In general, the oxidation reactions of these small molecules can be divided into SAORs and ESRs according to their applications. In terms of SAORs, small molecules (e.g., ammonia, urea and hydrazine) from human urine or chemical wastewater are applied as sacrificial agents to generate non-toxic CO₂ and N₂ at low theoretical potentials. This approach is thus a cost-effective way to remove ammonia, hydrazine and/or urea in wastewater, especially when those SAORs are coupled with HER. With regard to ESRs, small molecules such as alcohol, aldehyde, glucose, amine and sulfion are applied as substances to produce highly value-added chemical additives (e.g., formate, acetate, glycolic acid, glycerate, glucaric acid, 2,5-furandicarboxylic acid (FDCA), nitriles, S) that are extremely vital in the application

fields of chemical synthesis, medicine, printing and dyeing, and plastic industries. This strategy can even bring lots of economic benefits (namely to efficient and costeffective yield of high value-added chemicals or fuels) once it is combined with renewable electricity.

2.2 Reduction reactions of small molecules

Cathodic reduction reactions of small molecules in the coupled electrolyzer systems often involves HER, ORR, CO₂RR, NRR and others. To have the right choice of these reactions, one has to bear in mind that only those with fast reaction rates, low energy cost, high selectivity into high-value products, and simply operating environment are considered to be promising for coupled electrolyzer systems. Taking HER, a well-known half-reaction of water splitting as an example, it converses (renewable) energy into H_2 with a high efficiency and can meet demands for multiple applications. Another example is ORR that use cheap O_2 as the reactant. Once it is coupled with other anodic oxidations reactions (e.g., ammonia/hydrazine/urea/alcohol oxidation), fuel cells can be fabricated. Note that ORR can also generate valuable H₂O₂ if only two electrons are involved. For CO₂RR, CO₂ is electrochemically reduced into different chemicals such as CO, CH₄, HCOOH, CH₃OH, C₂H₅OH and C₂H₄.^[39-41] For NRR, N₂, the most earth-abundant gas, is electrochemically reduced to NH₃ under mild conditions compared to a traditional Haber-Bosch approach.^[15] Besides, some promising reduction reactions with appropriate potential from biomass-derived small molecules can not be neglected. For example, HMF as one typical biomass-derived small molecule can be reduced to valuable 2,5-Bishydroxymethyltetrahydrofuran (DHMTHF) via a cost-effective approach.

2.3 Design strategies of electrocatalysts

In the practical application, the kinetics of oxidation and reduction reactions of small molecules are normally known to be sluggish, considering their evolution pathways involve multiple electrons transfer. Prior to integrating these reactions to construct coupled systems for various applications, their conversion efficiencies need to be improved. To accelerate reaction kinetic of these reactions, efficient catalysts are highly needed, especially those can determine effectiveness and selectivity of both cathodic reduction and anodic oxidation reactions.^[1] In this context, some strategies have been employed to produce advanced catalysts. The proposed methods mainly

include doping, alloying, defect generation, heterostructure or special nanostructure formation. Using these approaches, electronic structures of these catalysts are further optimized and the adjusted *d*-band center then modulates the adsorption energy of key intermediates generated during these reactions. In other words, the intrinsic activity of these catalysts is markedly enhanced. Together with increased specific areas (more exactly more exposed active sites), improved electron transfer processes are obtained. Note that OER is the competing reaction toward small molecule oxidation reactions, designing suitable catalysts, which can boost small molecule oxidation reactions but restrain the OER, is helpful for industrial development of coupled electrolyzer.

2.4 Coupled electrolyzers

Coupled electrolyzers refer to combined electrochemical systems where anodic oxidation reactions of small molecules are integrated with cathodic reduction reactions (e.g., HER, ORR, CO₂RR, NRR and others). The choice of these reactions leads to various functions of coupled electrolyzer cases, eventually meeting the demands of various applications. For example, a SAORs/ESRs/HER system stands for a coupled electrolyzer system consisting of SAORs or ESRs and HER. Due to the replacement of OER with SAORs/ESRs, this system is expected to show lower cell voltage than that of overall water splitting (OWS) during H₂ production. In the case of a SAORs/ESRs|ORR system, it is expected to own high electricity output, along with efficient removal of pollutants (e.g., ammonia, urea and hydrazine) from wastewater. As the ESR coupled with CO₂RR, NRR, NO₃RR, reduction of R-NO₂ and HMF, generation of valuable products are highly possible at both anode and cathode. Beside these redox coupled reactions for small molecules, the configuration, applied membrane, concentration of small molecules and pH of electrolyte also play important roles in modulating the performance of coupled electrolyzers. Importantly, the oxidation reactions coupled with reduction reactions should be matched in thermodynamic and kinetic.

3. Performance of oxidation reactions of small molecules

3.1 Sacrificial agent oxidation reaction (SAORs)

As a promising strategy, SAORs addresses the issues of OER during water splitting such as low activity and poor stability. Advanced catalysts have been designed and applied for SAORs and meanwhile to improve the efficiency of H_2

generation. In this session, some typical SAORs are summarized, including design strategies and characterization of reported SAORs catalysts accompanying their reaction mechanisms and their performance.

3.1.1 Ammonia oxidation reaction (AOR)

Liquid ammonia, a pollutant from industrial and municipal wastewater, has been regard as a promising sacrificial agent for SAORs. This is because it is easy to be stored and transported with a high energy density of 4.3 KWh kg⁻¹. In belief, an ammonia oxidation process ($2NH_3 + 6OH^- \rightarrow N_2 + 6H_2O + 6e^-$, theoretical potential of -0.77 V vs. RHE) produces electric energy without the emission of greenhouse gas $CO_2^{[37.39[42-44]}$. Meanwhile, the NH₃ pollutant in wastewater can be effectively removed.

Two mechanisms have been proposed and widely accepted for AOR. One is socalled Gerischer-Mauerer (G-M) mechanism (NH₃ \rightarrow NH₂^{*} \rightarrow NH^{*} \rightarrow N₂H_{x+y}^{*} \rightarrow N₂), another is so-named Oswin-Salomon (O-S) mechanism ($NH_3 \rightarrow NH_2^* \rightarrow NH^* \rightarrow N^* +$ $N^* \rightarrow N_2$). It has been reported that Pt and Ir-based catalysts exhibited high activity toward AOR and followed the G-M mechanism.[45-48] Recently, 3D coral-like Pt nanowires was designed to accelerate the AOR, which exhibited a superior oxidation current density to state-of-the-art Pt/C catalyst, attributed to its optimal electronic structure caused by the unique nanostructure to facilitate G-M process.^[46] Another case reported by Siddharth and coworkers demonstrated the introduction of trace Ir could enhance the adsorption of NH_x on Pt (100) to improve the AOR activity (Figure 3a and 3b), and the addition of Ni(OH)₂ alleviate the poisoning of N intermediate to increasing the stability of Pt (Figure 3c).^[49] As to G-M mechanism, it worth noting that active OH species in alkaline electrolytes or adsorbed OH has not been clearly identified until the adsorption of reactive OH species on the Pt (100) facet has been revealed using ab into molecular dynamics (AIMD).^[45] Consequently, adsorbed OH (OH_{suf}) has been recognized as the active species during the NH₃ dehydrogenation.

Different from Pt and Ir-based catalysts, Cu-based samples have showed excellent AOR activity *via* the O-S mechanism.^[24, 43, 50-51] For example, the reaction mechanism of AOR on a Ni-Cu-Fe oxyhydroxide (Ni-Cu-Fe-OOH) was testified as following an O-S mechanism ("N+N" mechanism) (**Figure 3d**),^[51] where the doping of CuFe into NiOOH promoted electron accumulation around oxygen atoms (**Figure 3e**). This Cu-based catalyst required only a potential of about 0.7 V vs. RHE to reach a current density of about 60 mA cm⁻² (**Figure 3f**), ammonia removal efficiency

arrived at nearly 95.1% after 24 h continuous operation, and the faradaic efficiency was dependent on the applied potential (**Figure 3g**). On the other hand, the effect of NH₃ concentration on AOR performance showed removal efficiency of NH₃ sharply decreased from around 55% to 10% as the concentration of NH₄Cl increased from 100 to 500 mM after the operation for 12 h (**Figure 4h**), mainly attributed to active sites was easily covered and poisoned by NH₃ in high concentration.



Figure 3. (a) LSV curves of Pt NCs/C, Ir-decoreated Pt NCs/C, Ir and Ni(OH)₂ -decorated Pt NCs/C in 0.1 M KOH with 0.1 M NH₃ solution. (b) Gibbs free energy diagram for AOR. (c) Chronoamperometric test at 0.60 V. Reproduced with permission.^[47] Copyright 2020, Elsevier. (d) Optimized supercell model and schematic illustration of ammonia oxidation process for Ni-Cu-Fe-OOH catalyst. (e) Gibbs free energy of N+N mechanism for Ni-Cu-OOH and Ni-Cu-Fe-OOH, the inset figure shows the Gibbs free energy diagram of G-M mechanism and N+N mechanism for Ni-Cu-Fe-OOH. (f) CV curves in 0.5 M NaOH with and without 55 mM NH₄Cl. (g) Faradaic efficiency and ammonia removal efficiency under different potential. (h) Removal efficiency of ammonia at different ammonia concentrations. Reproduced with permission.^[51] Copyright 2021, Wiley-VCH.

3.1.2 Urea oxidation reaction (UOR)

Electrooxidation of small urea (CH_4N_2O) molecule into CO_2 , N_2 and H_2O in alkaline media is known to happen at a low standard electrochemical potential (-0.46

V vs. RHE), significant lower than that of OER (0.4 V vs. RHE).^[25, 52] On the other hand, urea is regarded as a crucial pollutant in industrial wastewater and human urines, which thus threatens human and animal health.^[53] Compared to traditional chemical oxidation and biohydrolysis, electrochemical urea oxidation reaction (UOR: $CO(NH_2)_2 + 6OH \rightarrow CO_2 + N_2 + 5H_2O + 6e^{-}$) has been proved to be a more essential and efficient way to remove urea in the aquatic environment. However, UOR processes a sluggish pathway since transfer of six electrons is involved.^[25] Therefore, constructing excellent UOR catalysts based on earth-abundant elements to accelerate the kinetic of UOR is of great urgence and highly valuable.

The Ni-based catalysts have been firstly reported to possess excellent UOR activity.^[25, 54] Later on, other transitional metals such as Co,^[55-57] Fe,^[52, 58] Mn^[59-60] and Mo-based^[61-62] catalysts and some nitrides^[63], phosphide^[56, 64] sulfide^[65] and oxide^[66] also have been applied for UOR (Table 2), exhibiting varied activities. Meanwhile, the reaction mechanisms of UOR on the Ni-based catalysts have been widely studied. It has been generally accepted that in alkaline electrolyte Ni is firstly oxidized to Ni(OH)₂ and further to NiOOH, which is main active species for UOR.^[54] The pathway of UOR on Ni-based catalysts is generally suggested as $*CO(NH_2)_2 \rightarrow *CO(NH.NH_2)$ \rightarrow *CO(NH.NH) \rightarrow *CO(NH.N) \rightarrow *CO(N₂) \rightarrow *CO(OH) \rightarrow *CO(OH.OH) \rightarrow *COO.^[67] Note that although varied barrier energies are involved in these converse steps, the rate-determining step (RDS) of UOR is the desorption of *COO intermediate. Unfortunately, adsorption of *COO intermediate on NiOOH is strong, resulting in limited UOR activity of most Ni-based catalysts. In this context, how to reduce *COO adsorption on Ni-based catalysts has been taken into account further to develop these catalysts. For example, their electronic structures have been adjusted to reduce the adsorption energy of *COO intermediate on NiOOH and eventually to enhance related reaction kinetics. Some effective methods to modulate such electronic structures include nanostructure,^[50, 53, 57-58] doping,^[13, 68-69] defect generation,^[70-71] and interface engineering^[59-60, 65, 72].

As far as doping is concerned, it refers to the introduction of metallic heteroatoms with high valence states (e.g., V, Cr, Mo and W) into Ni-based catalysts with an aim to effectively modulate electronic structure of Ni active sites. For example, a tungsten-doped Ni (Ni-WO_x) catalyst has been synthesized and applied for UOR. It required only a potential of 1.4 V vs. RHE to deliver a higher current density of 100 mA cm⁻², 273 mV less than that of OER (**Figure 4a**).^[13] The introduction of W

heteroatom was believed to increase the number of Ni³⁺ active sites *via* charge redistribution, which facilitated electrons transfer from Ni site to W site. During the UOR, the electron-withdrawing group (C=O) inside urea molecules is preferable to be adsorbed in the negative region on the Ni-WO_x surface, while electron-donating group (-NH₂) in the positive region, eventually accelerating the urea decomposition (**Figure 4b**). In another study, a Cr-doped CoFe layered double hydroxides (CoFeCr LDH/NF) catalyst has been employed for UOR.^[58] The first oxidation step of this CoFeCr LDH/NF catalyst was assumed to be the quick oxidization of Cr into Cr³⁺, followed by further oxidation of Cr³⁺ into Cr⁶⁺. It was found the formation of highly active Fe³⁺/Co³⁺ was boosted by a strong ability of capture electrons. As a result, the CoFeCr LDH/NF catalyst showed a wonderful activity for UOR (e.g., a potential of as low as 1.305 V vs. RHE at a current density of 10 mA cm⁻²).

Constructing abundant oxygen vacancies is another efficient way to enhance the UOR activity of transition metal-based catalysts. For instance, oxygen vacancy-rich NiMoO₄ nanosheets have been synthesized through a hydrothermal synthesis approach coupled with heat treatment at N₂ atmosphere. In 1 M KOH this catalyst only required a potential of 0.6 V vs. RHE to deliver a current density of 249.5 mA cm⁻². Such a high UOR activity was mainly derived from the introduction of rich oxygen vacancies, which increased the conductivity of the catalyst to promote electron transfer. More importantly, these oxygen vacancies activated the adsorption of urea on the surface of catalysts since the electrons adjacent to oxygen vacancies were delocalized. Additionally, introduced oxygen vacancy can optimize geometric structure to further boost UOR. For example, the crystal structure of an oxygen vacancy rich V-doped Ni(OH)₂ (O_{vac}-V-Ni(OH)₂) catalyst (**Figure 4c**) was changed from square pyramidal VO₅ to tetrahedral VO₄, due to the formation of plenty of oxygen vacancies after the V doping.^[71] The change of geometric structure modulated electronic structure of catalysts, resulting in high UOR activity (**Figure 4d**).

Constructing heterostructures has been also recognized as a powerful strategy to promote UOR activity, namely through generating new active sites. It has been reported that Schottky heterojunctions derived from combining a conductive metal with a semiconductor create local electro/nucleophilic regions, which will facilitate the adsorption of electron-donating -NH₂ group and electron-withdrawing C=O group for urea molecules. Consequently, these heterostructures are beneficial for the urea decomposition.^[65, 73-74] In addition, this Schottky heterojunction can accelerate

interfacial electron transfer, resulting in enhancing the UOR performance. For instance, a CoS₂/MoS₂ Schottky heterojunction exhibited higher UOR activity than both individual CoS₂ and MoS₂.^[65] The authors attributed such high UOR performance or the accelerated urea decomposition to increased apparent electron transfer processes from metallic CoS_2 to semiconductive MoS_2 on the heterojunction interface. Similarly, a CoMn/CoMn₂O₄ Schottky heterojunction structure showed a potential of as low as 1.32 V vs. RHE at a current density of 10 mAcm⁻² towards UOR, thanks to a self-driven electron transfer process from metallic CoMn component to the semiconducting CoMn₂O₄.^[59] In another study, a Ni/W₅N₄/NF Mott-Schottky heterojunction in the form of nano-microspheres has accompanied with an obviously enhanced electron transfer from metallic Ni to W_5N_4 (Figure 4e, f).^[72] As to this catalyst, only a potential of 1.34 V vs. RHE was needed to reach a current density of 10 mA cm⁻² during UOR, while a potential of 1.51 V vs. RHE was required for OER under identical conditions. In addition, an industrial-scale current density of 1000 mA cm⁻² was kept well at 1.6 V vs. RHE, much lower than that (1.88 V vs. RHE) for OER (Figure 4g).

Apart from as-mentioned strategies to tune electronic structures of catalysts, creating new reaction pathways has been testified as an efficient approach to improve the UOR performance. For example, a nickel ferrocyanide (Ni₂Fe(CN)₆) catalyst has been applied to establish a novel tandem mechanism:^[52] without the involvement of NiOOH species. This mechanism was proposed to include both a chemical process $(CO(NH_2)_2 + H_2O \rightarrow CO_2 + 2NH_3)$ and an electrochemical process $(2NH_3 + 6OH \rightarrow N_2 + 6H_2O + 6e)$. According to the density functional theory (DFT) calculations for UOR on the Ni₂Fe(CN)₆ catalyst, urea is believed to be decomposed into NH₃ on the Ni sites during the chemical process. In 1M KOH, the potential of UOR for this catalyst was located at 1.35 V vs. RHE when the current density was 100 mA cm⁻². Additionally, UOR activity was affected by the pH of electrolyte. For example, Ni₂Fe(CN)₆ showed the different reaction rate with respect to different pH values, toward the UOR. On the other hand, higher concentration of urea would poison the surface of catalysts, causing the inferior performance toward UOR.^[59]



Figure 4. (a) The comparison of LSV curves. (b) Charge density difference for Ni-WO_x. Reproduced with permission.^[13] Copyright 2021,Wiley-VCH. (c) The cartoon schematic structure configuration of VO₅ and VO₄ and corresponding effects on adsorbates. (d) LSV curves in 1 M KOH with 0.33 M urea. Reproduced with permission.^[71] Copyright 2023,Wiley-VCH. (e) HRTEM image of Ni/W₅N₄. (f) Energy band diagram of metallic Ni and W₅N₄ with Mott Schottky interface. (g) The comparison of polarization curves for UOR and OER of Ni/W₅N₄/NF. Reproduced with permission.^[72] Copyright 2022, Elsevier.

3.1.3 Hydrazine oxidation reaction (HzOR)

Hydrazine (N₂H₄) oxidation reaction (HzOR) - N₂H₄ + 4OH⁻ \rightarrow N₂ + 4H₂O + 4e⁻ is a promising candidate to replace OER due to its ultralow theoretical potential (-0.33 V vs. RHE), ^[26] HzOR involves 4-electron transfer pathway without any emission of greenhouse gas CO₂. The combination of HzOR with HER is thus ideal for effective H₂ production, and meanwhile the removal of hydrazine that is extremely valuable in wastewater treatment.

Recently, a series of catalysts based on transition metals have been applied for efficient HzOR, including nitride,^[12, 75-79] selenide^[80-81] and phosphide^[12, 82-85] (**Table 2**). Among them, doping foreign elements into transition metal nitride (TMN) has been

shown as an effective way to enhance the HzOR activity. For example, P and W codoped Co₃N nanowires (Co₃N NWAs) grown on a Ni foam (PW-Co₃N NWAs/NF) have been utilized as a HzOR catalyst.^[12] Since W and P atoms respectively occupied the partial sites of Co and N atoms of Co₃N, the charge redistribution was promoted. The desorption Gibbs free energy (Δ G) for *N₂ intermediate as the RDS of HzOR was calculated to 0.5 eV on the PW-Co₃N NWAs/NF catalyst, lower than that on a Co₃N NWAs/NF catalyst (**Figure 5a**). Thus only a potential of 127 mV vs. RHE was required to reach the current density of 600 mA cm⁻² on the PW-Co₃N NWAs/NF (**Figure 5b**). Similarly, V-doped Ni₃N nanosheets grown on Ni foam (V-Ni₃N NS) enhanced electron transfer from Ni to N₃^[75] thus facilitated the adsorption of anti-N₂H₄ molecule on the Ni-termination of Ni₃N. As a result, this V-Ni₃N NS catalyst showed a potential of as low as 2 mV vs. RHE at a current density 10 mA cm⁻² toward the HzOR.

Construction of TMN heterostructures is another crucial way to promote the HzOR activity where electronic structure can be modulated accompanied with more exposed active sites Namely, this strategy remains intrinsic active sites of a catalyst and also generates new sites at the heterostructure interface. For example, a hierarchical porous nanosheet Ni₃N-Co₃N heterostructure constructed on Ni foam (Ni₃N-Co₃N PNAs/NF) exhibited an excellent performance for HzOR.^[86] Its X-ray photoelectron spectroscopy (XPS) analysis confirmed that electrons transfer from Co to Ni. Meanwhile partial Ni is reduced and partial Co is oxidized on the Ni₃N-Co₃N heterostructure interface. Thus the N₂H₄ adsorption is boosted on electron-deficient Co active sites. As a result, this Ni₃N-Co₃N PNAs/NF catalyst exhibited a potential of -88 mV vs. RHE at a current density of 10 mA cm⁻² for HzOR. Especially, a potential of 200 mV vs. RHE was reached at an industrial-scale current density of 1000 mA cm⁻ ² (Figure 5c). In another case, a double-islands hybrid Ni-C (Ni-C HNSA) catalyst has been designed (Figure 5d),^[79] where Ni nanoparticles occupied one island for multi-stepped dehydrogenation (Figure 5e), while Ni@C sits at another island to improve the H* adsorption (Figure 5f). This catalyst required a potential of -20 mV vs. RHE to deliver a current density of 10 mA cm⁻² toward HzOR. Different from traditional metal/metal nitride heterostructures, an unsaturated nickel surface nitride encapsulated in a carbon shell (Ni-SN@C) has been also reported as a HzOR catalyst,^[76] where metallic Ni atoms and unsaturated Ni-N bonds promote electron redistribution, thus presenting a low potential of 16.8 mV vs. RHE for a current

density 10 mA cm⁻².



Figure 5. (a) The free energy profiles of HzOR. The inset in (a) are the most stable configuration of the each intermediate on the Co site. (b) LSV curves in 1.0 M KOH/0.1 M N₂H₄ electrolyte. Reproduced with permission.^[12] Copyright 2020, Nature. (c) IR-corrected LSV curves 1.0 M KOH/0.1 M N₂H₄ electrolyte. Reproduced with permission.^[86] Copyright 2020, Wiley-VCH. (d-f) HRTEM images of Ni-C HNSA. Reproduced with permission.^[79] Copyright 2021, Wiley-VCH.

3.1.4 Complete alcohol oxidation reactions

Complete alcohol oxidation reactions to produce CO₂ such as methanol oxidation reaction (MOR) and ethanol oxidation reaction (EOR) have been widely applied in direct methanol/ethanol fuel cells (DMFCs/DEFCs), stemming from the abundance of different alcohols at low price, easy storage and transport, and high energy density (e.g., 6 KWh kg⁻¹ for methanol and 8 KWh kg⁻¹ for ethanol).^[87-90] Multiple electron transfer is generally involved in complete alcohol oxidation reactions to deliver more electricity. For example, methanol and ethanol can be fully oxidized into CO_2 , releasing 6 (CH₃OH + 6OH \rightarrow CO₂ + 6H₂O + 6e⁻) and 12 (CH₃CH₂OH + 12OH \rightarrow $CO_2 + 9H_2O + 12e^{-}$) electrons, respectively. In these cases (namely these C1 reaction pathways), noble metals such as Pt, Pd-based catalysts are generally regarded as the most active electrocatalysts.^[91-92] However, they are expensive and easily poisoned by *CO intermediate. In this regard, multi active sites are introduced into noble metal catalysts to further improve sluggish kinetic and limit the poisoning effect of different alcohol oxidation reactions. The extensively tried approaches include the alloy formation and the construction of core@shell catalysts. Based on these specific nanostructures, the free energy barriers for the adsorption of key intermediates are expected to be lowered, leading to their optimized adsorption on noble metal

catalysts. For example, the tensional strain formed in Au@PdPt lowered the free energy barriers for the formation of key intermediates and decreased the CO adsorption energy, thus exhibited the outstanding MOR activity (e.g., a mass activity of 4.83 mA mg⁻¹). ^[93]

High-entropy alloys, composed by five or more neighbor elements with equal concentrations, have shown outstanding activity and stability toward complete alcohol oxidations, owing to existing synergistic effects among multi active sites (or different atoms). For example, a Pt-group high-entropy alloy (PGM-HEA) with six neighbored elements (Ru, Rh, Pd, Os, Ir and Pt) exhibited superior EOR activity in comparison to commercial Pd/C, Pt/C and Pd black.^[94] This was the first report about the application of PGM-HEA toward EOR. Such high performance was attributed to the optimized surface configuration *via* the introduction of adjustable six components. In more detail, PtPdRh alloy was believed to boost the oxidation reactions of poising species, Ir sites adjusted the adsorption strength of intermediates, Ru sites enhanced the adsorption of OH⁻, facilitating CO_{ads} oxidation at a lower potential, while Os sites accelerated the breakage of the C-C band. Note that noble metals are rare and expensive, exploring non-noble metal electrocatalysts with high performance toward alcohol oxidation reactions is of great significance.

In the section of SAORs, the products at anode such as CO_2 and N_2 exhibit low economic value in general, but are of great importance for removing related pollutant in wastewater. Note that the concentration of substrate for AOR, UOR or HzOR is increased to a high enough level in electrolyte, it is possible for promising application in direct ammonia fuel cells (DAFCs), direct urea fuel cells (DUFCs) and direct hydrazine fuel cells (DHzFCs).

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Catalysts	Electrolyte	$E_{SAORs}(V vs.)$	Coupled	$V_{Cell}(V@mA cm^{-})$	Ref.
	(Substrate + 1.0	RHE@mA cm ⁻²)	electrolyzer	²)	
	M KOH)				
Coral-like Pt	0.05 M	-0.37 V			[46]
nanowires	$(NH_4)_2SO_4$	vs.SCE@0.167			
V _o -rich CuO	1.0 M ammonia	0.6 V vs.		4	[50]
		Hg/HgO@120			

 Table 2. Performance of recently reported electrocatalysts for SAORs and related coupled electrolyzers.

Ni-MOF nanosheet	0.33 M urea	1.36@10			[95]
Oxygen vacancy-	0.5 M urea	0.6 V vs.			[70]
rich NiMoO ₄		Ag/AgCl@249.5			
Ni-MoN NAMs	0.33 M urea	1.36@100	UOR HER	1.41@20	[96]
O _{vac} -V-Ni(OH) ₂	0.33 M urea	1.47@100	UOR HER	1.5@10	[71]
Ni ₂ Fe(CN) ₆	0.33 M urea	1.35@100	UOR 2e ⁻ ORR	0.58@10	[52]
MnO ₂ /MnCo ₂ O ₄ /Ni	0.5 M urea	1.7@368	UOR HER	1.85 @60	[60]
$Zn_{0.08}Co_{0.92}P$	0.5 M urea	0.6 V vs.	UOR HER	1.38@10	[56]
		SCE@115			
Ni ₃ N	0.33 M urea	1.35@10	UOR HER	1.44@10	[63]
nanosheets/CC					
1% Cu:α-	0.33 M urea	1.405@100	UOR HER	1.49@10	[97]
Ni(OH) ₂ /NF					
Ni ₂ P NF/CC	0.5 M urea	0.477V vs.	UOR HER	1.35@50	[64]
		SCE@100			
O-NiMoP	0.5 M urea	1.41@100	UOR HER	1.36@100	[61]
Ni-Mo nanotube	0.1 M urea	1.36@10	UOR HER	1.43@10	[62]
CoFeCr LDH/NF	0.33 M urea	1.305@10	UOR HER	1.329@10	[58]
Ni-WO _x	0.33 M urea	1.4@100	$UOR \ CO_2 RR$	2.16@100	[13]
CoMn/CoMn ₂ O ₄	0.5 M urea	1.32@10	UOR HER	1.68@100	[59]
CoS_2/MoS_2	0.5 M urea	1.29@10	UOR HER	1.29@10	[65]
Ni/W ₅ N ₄ /NF	0.5 M urea	1.34 V@10	UOR HER	1.33@10	[72]
V-Ni ₃ N/NS	0.1 M hydrazine	0.116@500	HzOR HER	0.264@50	[75]
Ni-C HNSA	0.1 M hydrazine	-0.02@10	HzOR HER	0.4@200	[79]
Ni-SN@C	0.1 M hydrazine		HzOR HER	0.366@10	[76]
Ni ₂ P/NF	0.5 M hydrazine	0.018@200	HzOR HER	1@500	[82]
$CoSe_2$ nanosheet	0.5 M hydrazine	-0.017@10	HzOR HER	0.164@10	[80]
Fe-CoS ₂	0.1 M hydrazine	0.129@100	HzOR HER	0.95@500	[3]
3D NiCoSe ₂ /NF	0.1 M hydrazine	-0.7 V vs.SCE (one	HzOR HER		[81]
		set)			
Cu ₁ Ni ₂ -N	0.5 M hydrazine	0.0005@10	HzOR HER	0.24@10	[78]

RuP ₂ -N, P dual-	0.3 M hydrazine	-0.07@10	HzOR HER	0.227@100	[84]
doped carbon					
porous microsheets					
PW-Co ₃ N	0.1 M hydrazine	-0.055@10	HzOR HER	0.607@200	[12]
NWA/NF					

3.2 Electrochemical synthesis reaction (ESRs)

In addition to SAORs, ESRs are also promising candidates as the OER replacement to decrease energy consumption for H_2 production. Different from SAORs which often yields low valuable products, ESRs can converse small molecules to value-added chemicals without greenhouse CO_2 emission, while accompanying with a low efficiency. In this section, the design and construction of effective catalysts for ESRs using different strategies are thus summarized.

3.2.1 Glucose oxidation reaction

Glucose is a common biomass-based carbohydrate. Its oxidation reactions provide several valuable products such as HMF, sorbitol, gluconic acid (GNA) and glucaric acid (GRA). Among those products, GRA is the most valuable biomassbased chemical for industrial applications such as synthesis of polymers, food and pharmaceuticals.^[98] It has been predicted the global market share of GRA will arrive at \$1.3 billion by 2025.^[32] Several traditional methods exist for glucose oxidation, including chemical oxidation and microbial fermentation methods. For these methods, toxic oxidants are applied during the reaction, bringing potential risks. Moreover, these methods have low selectivity of GRA generation. Different from them, electrooxidation (theoretical potential: -0.78 V vs. RHE) has been shown to be a more promising way to transform glucose to GRA, due to its high selectivity and its beneficial economic effect.^[32, 99-102] For example, NiFeO_x grown on Ni foam (NiFeO_x -NF) exhibited a low onset potential of 1.13 V vs. RHE in 1 M KOH + 0.1 M glucose (Figure 6a) and the yield of GRA was 83.3% after 2 h operation confirmed by 2D-HSQC nuclear magnetic resonance (NMR) and liquid chromatograph-mass spectrometer (LC-MS), and no C-C bond cleavage revealed by in situ ATR-FTIR during glucose oxidation. (Figure 6b).^[32] Additionally, the effect of Pt oxidation state on selectivity toward glucose oxidation was evaluated via high-pressure liquid chromatograph (HPLC) combined high-pressure anion exchange chromatograph

(HPACE), which could quantify all intermediate products.^[99] It was found Pt⁰ only favored dehydrogenation of primary alcohol while PtO_x showed bifunction for dehydrogenation of primary alcohol and oxidation of aldehyde (**Figure 6c**). However, more efforts are highly required to separate complex products in this case.



Figure 6. (a) LSV curves in 1 M KOH with 100 mM glucose. (b) Concentration and oxidation products versus time at 1.3 V. Reproduced with permission.^[32] Copyright 2020, Nature. (c) Reaction pathway for glucose oxidation on Pt⁰ and PtO_x catalysts in neutral media. Reproduced with permission.^[99] Copyright 2023, Wiley-VCH. (d) LSV curves in 1 M KOH with and without 1mM BA. (e) Substrate scope of primary amines electrooxidation to nitriles on NiSe catalyst in 1M KOH and 1 mM primary amines at 25 , yields are determined by gas chromatography, FEs are displayed in parentheses. Reproduced with permission.^[103] Copyright 2018, Wiley-VCH.

3.2.2 Amine oxidation reaction

Electro-oxidation of amine into nitrile is a very important reaction with theoretical potential of -0.77 V vs. RHE.^[33-34] It is unlike traditional chemical oxidation of amine, where toxic cyanides or strong oxidants are required. Ni-based catalysts have been widely explored for benzyl amine oxidation reaction (BAOR).^[33, 103-107] For example, the NiSe nanorod arrays displayed obviously oxidation current starting at 1.34 V vs. RHE with the addition of BA ^[103] (**Figure 6d**), attributed to highly active redox species Ni /Ni toward BAOR. In addition, this catalyst also exhibited high compatibility towards other aromatic and aliphatic primary amines with high yield (>94%) (**Figure 6e**). To improve chemical oriented conversion, a series of transition

metal (e.g., Fe, Co, Mn, Cu) doped α -NiOOH were constructed for BAOR.^[107] It was testified that Mn doped α -NiOOH exhibited the most excellent activity and selectivity (e.g., faradaic efficiency of 96% and benzonitriles selectivity \geq 99%). DFT calculation demonstrated Mn doping altered the adsorption site from Ni to Mn thus promoted the adsorption of amine, meanwhile reduced ΔG value of the second H rearrangement in the assistant of the active oxygen on the adjacent Ni site. In addition, heterostructure catalysts also were suggested to boost the BAOR. For instance, a heterojunction catalyst composed of Mo_{0.8}Ni_{0.2}N nanosheets and Ni₃N nanoparticles (Mo_{0.8}Ni_{0.2}N-Ni₃N) exhibited a wonderful activity toward BAOR.^[104] Due to electron transfer from Ni₃N to Mo_{0.8}Ni_{0.2}N, the accumulation of OH* on Ni₃N, was greatly improved verified by electron paramagnetic resonance (EPR) and upshift of d-band center of Mo_{0.8}Ni_{0.2}N-Ni₃N. The OH* species on Ni₃N facilitated the formation of highly active NiOOH species and restructured the surface of heterostructure, resulting in the superior BAOR activity.

3.2.3 Selective alcohol oxidation reaction

3.2.3.1 Selective MOR

Compared to complete MOR, selective MOR (CH₃OH + 5OH \rightarrow HCOO + 4H₂O + 4e⁻) appears to more interesting. On the one hand, selective MOR has a theory potential of 0.103 V vs. RHE, lower than OER,^[27] potentially leading to reduced energy consumption. Meanwhile, selective MOR provides value-added chemicals such as formate but without emitting greenhouse gas CO₂. Formate (1300 \$/ton) is a vital chemical intermediate and has frequently used in pesticide, medical, electroplating, printing and dyeing industries.^[88] In short, development of selective MOR to produce formate is highly beneficial in addition to efficient hydrogen production during hybrid water splitting.

It is well acknowledged that noble metals such as Pt-based catalysts are excellent MOR catalysts.^[108-109] Unfortunately, the selectivity of these Pt-based catalysts is very limited; their price is high; their stability is poor; they are easy to be poisoned by CO. In this context, non-noble metal catalysts, particularly Ni-based catalysts have been proposed for selective MOR recently (**Table 3**) ^[110] where NiOOH is generally considered as main active site.^[111] For example, Ni(OH)₂ nanosheet arrays prepared on a nickel foam (Ni(OH)₂/NF) acted as an effective anodic catalyst for selective MOR in a KOH solution.^[112] According to common catalytic reaction mechanism of Ni-based catalysts,^[40, 110, 113] it was stated that Ni(OH)₂ firstly was oxidized to NiOOH, then

oxidized methanol into formate meantime NiOOH was reduced to Ni(OH)2. The calculated Gibbs free energy diagrams well supported such a statement. The HCOOH formation was thermodynamically favorable during selective MOR on this catalyst, where a lowered ΔG value (-0.95 eV) was noticed for the conversion of HCOOH into COOH, while an enhanced energy barrier (0.88 eV) occurred during the conversion of HCOOH to COOH. Note that HCOOH is easily changed into formate in alkaline media, but further oxidation of HCOOH was well restricted on this catalyst (Figure 7a). At a current density of 100 mA cm^2 , the faradaic efficiency of selective MOR was nearly 100%. In another case, Ni-based metal organic framework (Ni-MOF) denoted as Ni-NF-Af, exhibited a larger surface area and more Ni-OH bonds to enhance NiOOH active sites. On this Ni-NF-Af catalyst, a potential of 1.388 V vs. RHE was realized even at an industrial scale current density of 500 mA cm⁻² (Figure 7b). Meanwhile, this catalyst showed superior stability. The current density retained 81.2% of its initial value after 5 h operation at 1.38 V vs. RHE. Simultaneously, the potential was only increased 30 mV during the electrolysis with a constant current density of 100 mA cm⁻² for 5h (Figure 7c).



Figure 7. (a) Gibbs free energy diagrams for MOR. Reproduced with permission.^[112] Copyright 2020, Elsevier. (b) LSV curves with iR compensation. (c) Long-term stability test at 1.38 V or 100 mA cm⁻² for 5 h in 1.0 M KOH with 0.5 M methanol. Reproduced with permission.^[40] Copyright 2021, Wiley-VCH. (d) Schematic drawing of the synthesis route of NiTx-R. (e1-e4) Optimized structural models of oxyanions-doped NiOOH and pure NiOOH. Reproduced with permission.^[110] Copyright 2022, Nature.

To facilitate selective MOR, other elements have been introduced into Ni-based catalysts. In this way, additional active sites are probably created and meanwhile electronic structures of Ni-based catalysts can be adjusted, eventually resulting in optimized adsorption energy of key intermediates generated during MOR. In literature, some efforts have been devoted to realizing selective conversion of methanol into formate *via* the introduction of heteroatoms (e.g., P, S and Se) into Ni-

based catalysts. A series of Ni-metalloids (NiT_x-R, T=P, S and Se) have been synthesized on Ni foam (Figure 7d). Active species of NiOOH-TO_x were generated via electrochemical activation and surface reconstruction (Figure 7e). Calculations of adsorption energy and projected density of states (PDOS) disclosed NiOOH-PO_x exhibited higher OH* and CH₃OH adsorption, and stronger Ni-O covalency than both NiOOH-SO_x and NiOOH-SeO_x, resulting in a lower potential of 1.4 V vs. RHE at a current density of 400 mA cm⁻² in 1 M KOH + 0.5 M methanol. In another case of NiSe hollow nanocrystals deposited on carbon nanotubes (h-NiSe/CNTs), active sites (NiOOH and SeO_x) would be formed on the surface of NiSe toward MOR verified by in situ Raman experiments.^[114] Under the cooperation between NiOOH and SeO_x, this h-NiSe/CNTs catalyst exhibited an optimized adsorption energy to boost selective MOR. In addition, when Ni specie was partially replaced by Fe $(Ni_{0.75}Fe_{0.25}Se_2)$, the kinetics of the NiOOH formation was accelerated and electrochemically active surface area (ECSA) was enlarged,^[113] thus selective MOR activity was further boosted. One the other hand, designing various nanostructures for specialized exposed crystal facets is also very benefit for the selective MOR, such as carbon core/sheath catalyst (nanofibers@NiSe), which exhibited high performance for selective MOR into formate derived from more exposed (102) facets of NiSe.

Transitional metal nitrides and carbides have been explored to promote the selective MOR performance. For example, Mo-doped Co₄N nanoarrays (Mo-Co₄N) have been employed as a superior catalyst toward selective MOR.^[115] Its enhancement mechanism was attributed to the optimized electronic structure of Co active sites because of the introduction of Mo into Co₄N nanoarrays. In another case of Ni₃C catalyst, nearly 100% conversion efficiency for selective MOR and no byproduct of CO₂ were realized due to the formation of new active sites, as determined by means of in situ attenuated total reflection surface-enhanced infrared absorption (ATR-SEIRA) and infrared reflection absorption spectroscopy (IRAS).^[116]

3.2.3.2 Selective EOR

Selective EOR can be depicted as $CH_3CH_2OH + 5OH^- \rightarrow CH_3COO^- + 4H_2O + 4e^-$, where the C-C bond in ethanol molecule is reserved. The final product of this reaction is high value-add acetate without CO_2 emission. Acetate is a vital raw chemical and extremely useful in various fields such as synthesis of fiber vinyl, paint industry, buffer agents and so on.^[117] Up to now, noble metals, especially Pt-based materials are representative EOR catalysts.^[118-121] Yet, noble metal catalysts are prone

to complete EOR due to their stronger ability to cleavage C-C bonds than transition metal catalysts.^[120] To address this issue, a variety of design approaches have been presented for upgrade noble-metallic catalysts, mainly including dopant introduction and alloy formation. For example, a single-atom has been doped into sub-nanometer Pt nanowires (SA In-Pt NWs) to boost selective EOR. In this means, exposed Pt active sites were greatly enhanced, resulting in an excellent performance toward selective EOR.^[118] Similarly, a Ru-anchored porous Pt₃Ni alloy formed on Ni foam (Ru-Pt₃Ni/NiF) has been applied to push selective OER.^[120] In this case, Ru atoms promoted electron transfer from Ru to Pt, which strengthened adsorption of ethanol and meanwhile weakened adsorption of CH₃COOH on Pt active sites.

Some nonnoble metal-based materials have also been employed for selective EOR. In order to obtain outstanding performance, the design of heterostructure for these catalysts has been attracted extensive attention. For instance. Co(OH)₂@Ni(OH)₂ heterostructures exhibited a high activity of selective EOR in term of an oxidation potential of 1.389 V vs. RHE at 100 mA cm⁻² (Figure 8a).^[122] Such activity was contributed to enhanced high-valence Ni sites inside NiOOH obtained by Ni(OH)₂ partial oxidization to provide more low coordination states of Ni species. The calculated free energy profiles further confirmed that Co(OH)₂@Ni(OH)₂ possessed moderate ethanol adsorption strength and CH₃COOH desorption strength, resulting in its lower energy barrier of 1.64 eV for RDS (namely CH₃CH₂O to CH₃CHO) in selective EOR compared to CoOOH and NiOOH (Figure 8b). In the same situation, a NiOOH-CuO nano-heterostructure was constructed to enhance performance of selective EOR, where the interaction between two active species CuO and NiOOH resulted in charge redistribution from CuO to NiOOH. [123] This catalyst only required a potential of 1.347 V vs. RHE to reach a current of 200 mAcm⁻² in 1 M KOH + 1 M ethanol (Figure 8c). With aid of the results from energy barrier diagrams, CuO sites of NiOOH-CuO catalyst was the most feasible for selective EOR compared to CuO, NiOOH and NiOOH sites of NiOOH-CuO catalyst (Figure 8d).[123]



Figure 8. (a) LSV curves in 1 M KOH + 1 M ethanol electrolyte. (b) Gibbs free energy profiles of EOR. Reproduced with permission.^[122] Copyright 2022, The Royal Society of Chemistry. (c) LSV curves of 1 M KOH + 1 M ethanol electrolyte. (d) Gibbs free energy diagram of EOR. Reproduced with permission.^[123] Copyright 2023, Elsevier. (e) A probable mechanism of the synergetic effect for EGOR on the PdAg/NF catalyst. Reproduced with permission.^[124] Copyright 2021, Elsevier. (f) ¹H NMR spectra of products before and after 12 h GOR on Ni-Mo-N/CFC catalyst. Reproduced with permission.^[29] Copyright 2019, Nature. (g) Product concentration and glycerol conversion (stars) in relation to reaction time at 0.8 V based on HPLC analysis. (h) Proposed GOR pathway on the MoO_x/Pt catalyst. Reproduced with permission.^[125]Copyright 2021, Wiley.

3.2.3.3 Ethylene glycol oxidation reaction

Ethylene glycol oxidation reaction (EGOR) is very valuable which can oxidize ethylene glycol from waste plastic PET to highly valuable chemicals (e.g., formate and glycolic acid). With regard to this oxidation reaction, two reactions pathways are proposed according to the C-C breakage mechanisms. One pathway involves the C-C breakage and formic acid is the final product, following the reaction of $HOCH_2CH_2OH + 2OH^- \rightarrow HCOOH + 2H_2O + 2e^-$. In contrast, another pathway does not involve C-C breakage and final product is glycolic acid. The reaction can be expressed as HOCH₂CH₂OH + 2OH⁻ \rightarrow HOCH₂COOH + 2H₂O + 2e⁻. Although glycolic acid has the highest value since it can be used in various fields (e.g., cleaning agents, printing and dyeing, medicine),^[126-127] its selectivity is generally poor and HCOOH is main product of EGOR.^[128-129] In order to prohibit the C-C breakage to produce valuable glycolic acid, different catalysts have been designed and synthesized. For example, a PdAg alloy grown on a nickel foam (PdAg/NF) has been used a catalyst to selectively produce glycolic acid from EGOR.^[124] In this case (Figure 8e), electron-deficient Ag (Ag⁺) promoted electron transfer from Ag to Pd, while electron-enriched Pd was prone to adsorb ethylene glycol to form $O=*CCH_2OH$ intermediate. The crystal orbital Hamiltonian population (ICOHP) and PDOS calculation results further confirmed that addition of Ag strengthens the C-C bond and weakens the O-H bond, which were vital for the formation of glycolic acid. Thus this catalyst showed a satisfactory activity for selective ethylene glycol oxidation reaction in terms of a low potential of 0.57 V vs. RHE at 10 mA cm⁻² and a faradic efficiency of 92%. Therefore, it is high desirable to design advance catalysts which can not only consolidate C-C bond, but also activate O-H bond in ethylene glycol for accelerating value-added glycolic acid generating.

3.2.3.4 Glycerol oxidation reaction

Some efforts have been also devoted to glycerol oxidation reaction (GOR) since glycerol as a byproduct of biodiesel is cheap and well-resourced. Theoretically, conversion of glycerol to formate in alkaline media happens in the form of $C_3H_8O_3 +$ $8OH^- \rightarrow 3HCOOH + 5H_2O + 8e^{-}$, which needs a theoretical potential of -0.69 V vs. RHE.^[29] It is worth mentioning that the conversion of glycerol to C_3 products such as glycerate is a promising profitable pathway for GOR in that C_3 products possess high values.^[128] Therefore, various catalysts have been designed and synthesized for these different reactions. For formate production, a Ni-Mo-N nanoplate grown on carbon fiber cloth (Ni-Mo-N/CFC) showed a promising application with a 95% faraday efficiency, as proved by ¹H nuclear magnetic resonance spectroscopy (**Figure 8f**).^[29] In order to explore mechanism behind, a series of spinel oxides - ZnFe_xCo_{2-x}O₄ (x = 0, 0.4, 1.0, 1.4 and 2.0) have been employed for this kind selective GOR. It has been revealed that the ratio of Fe/Co, applied potential, glycerol concentration all affected the selectivity of formate production, indicating a complex synergistic effect for this reaction.^[130] For glycerate production, the optimization of glycerol is precondition. In this regard, a MoO_x/Pt catalyst has been synthesized for selective GOR, where Pt nanoparticles were trapped and confined at oxygen vacancies of MoO_x nanosheets.^[125] Due to electronic interaction between Pt and MoO_x, the adsorption of glycerol on Pt were sharply enhanced. Therefore, this catalyst exhibited a high selectivity of glycerate (in the range of 70-79%) rather than formate (**Figure 8g**). ^[125] It should be pointed out the electrolysis with longer time would decrease the selectivity of glycerate since it might further be oxidized to tartronate and oxalate (**Figure 8h**).

3.2.3.5 Other selective alcohol oxidation reactions

Oxidation of other alcohols (e.g., benzyl alcohol and isopropanol) has also been extensively studied. Benzyl alcohol electrooxidation reaction (BOR) has attracted much attention. Its theoretical potential is -0.35 V vs. RHE, much lower than that of OER.^[30] During BOR, benzoic acid and benzaldehyde are main products, which are widely used for chemical synthesis, food and medicine industry.^[131] To yield benzoic acid from BOR, several efficient catalysts have been reported. They were transition metals (e.g., Ni, Co, Fe) based oxides, hydroxides, and peroxides.^[30, 132-134] For example, a Au/CoOOH catalyst was constructed to boost BOR.[135] The enhancement mechanism was revealed by DFT calculations, where benzyl alcohol is firstly adsorbed and enriched at the Au/CoOOH interface via a σ - π bond, then prone to oxidization of benzyl alcohol into benzoic acid at the CoOOH active catalytic site. In further improve benzoic acid production, the quinary high-entropy FeCoNiAlMo alloy was designed and applied, since this type of materials could provide more active sites and faster charge transport, as well as optimize adsorption of key species.^[132] In this case, the adsorption of OH species was enhanced on Fe, Mo and Al sites, meantime the stronger adsorption of benzyl alcohol were found at Co and Ni sites for highly conductive FeCoNiAlMo/CNT catalyst, thus realized the superior activity via the cooperation effect among various active sites. Additionally, it was noted that benzaldehyde could form gem-diol intermediate in strong alkaline media, which was further oxidized to benzoic acid. Thus it was important to avoid the generation of gem-diol intermediate via limiting the hydration of benzaldehyde. Fortunately, a

specific NiO catalyst had realized the selectivity of benzaldehyde production of 100% based on the so-called salting-out effect,^[136] namely preventing hydration of benzaldehyde and increasing benzaldehyde aggregation were simultaneously occurred on the electrode surface *via* replacing strong KOH alkaline media with weak alkaline electrolyte of K₂CO₃.

Acetone generation from isopropanol oxidation reaction (IOR) have been also investigated. Acetone is a standard solvent as well as an important raw material in the explosive, plastic, drug fields.^[137] Due to the difficulty of IOR, noble metal (e.g., Pt, Pd, Ir and Rh) and their alloy catalysts^[137-140] are required. In this field, PdIr bimetallene nanoribbons (PdIr BNRs) with more active atoms and rich defects have been fabricated *via* a wet chemical synthesis method. Due to shifted down of *d*-band center for Pd induced by Ir, the adsorption and conversion of isopropanol on Pd active sites were significantly promoted. As a result, this catalyst only required a low potential of 0.38 V vs. RHE to produce a current density of 10 mA cm⁻² for IOR. Frankly speaking, there are no efficient catalysts except Pd-based catalysts for IR, more efforts should be devoted in this valuable field in further.

In belief, for the simple alcohol such as methanol and ethanol, transitional metal Ni- and Co-based catalysts are preferred, while for polyhydric alcohols and multicarbon alcohols, noble metal Pd- and Pt-based catalysts are more suitable. Meanwhile, it is a grand challenge to avoid over oxidation of alcohol to remain high yield of valuable products (eg., acetate, glycolic acid, glycerate and benzaldehyde).

3.2.4 Aldehyde oxidation

Integration of 5-hydroxymethylfurfural oxidation reaction (HMFOR) appears promising due to the sustainability and environmentally friendliness of HMF, easily obtained from C₅ and C₆ sugars, polysaccharides and plant fiber.^[141] Meanwhile, during HMFOR multiple products can be produced, including 2,5-diformyl furan (DFF), 5formyl-2-furancarboxylic acid (FFCA), 5-hydromethyl-2-furancarboxylic acid (HMFCA) and 2,5-furandicarboxylic acid (FDCA).^[142-143] Among them, FDCA is the most important biobased feedstock to generate polyethylene furan dicarboxylate (PEF), one of the most promising plastics due to its outstanding performance in hard heat condition.^[144-145] Development of FDCA generation from electrochemical HMFOR might be helpful to remit the problem of plastic pollution. In general, the conversion of HMF into FDCA is a 6-electron transfer process with sluggish kinetics (HMF + 6OH \rightarrow FDCA + 4H₂O + 6e[°]), although its theoretical potential is -0.53 V vs. RHE, much lower than that of OER.^[146] On the other hand, this HMFOR can involve two pathways, so-called the HMFCA or DFF route (**Figure 9a**).^[147]

To perform FDCA production from HMFOR, transition metal-based catalysts, especially Ni-based catalysts have been wildly studied.^[147-153] For example, a nickel boride alloy (Ni_xB) featuring a large surface area, exhibited a wonderful performance, such as a low potential of 1.45 V vs. RHE to deliver a current density of 100 mA cm⁻², a faradaic efficiency of nearly 100%, and the selectivity of 98.5% for the FDCA production (Figure 9b).^[147] Moreover, the production of DFCA though HMFCA route (pathway 1) was determined by electrochemistry-coupled attenuated total reflection infrared (EC-ATR-IR) spectroscopy (Figure 9c). In contrast, the oxidation of HMF to FDCA through a DFF route (pathway 2) was reported on Ni nanosheet vertically anchored carbon paper (Ni(NS)/CP).^[152] In this case, small crystal grain sizes of Ni(NS) where rich edges facilitate the oxidization of Ni to form Ni^{δ^+} (δ = 2-3) were beneficial for the adsorption and transformation of DFF, which is contributed to such a superior HMFOR performance(an onset potential of 1.33 V vs. RHE and a FDCA yield of 99.4%, Figure 9d). Additionally, Ni-based catalysts are also effective for the OER, especially at high potential and/or large current density, which was devoted to reducing the FE of FDCA and limiting the industrial application for HMFOR. How to enhance HMFOR meanwhile suppress OER at industrial level is much vital for practical application. In the case of the Ni-Cu/NF catalyst, active Cu not only improved the adsorption of HMF but deteriorated the RDS of OER (OH* \rightarrow O*).^[153] As a result, this catalyst only required 1.5 V vs. RHE to realize an industrial-scale current of 1000 mA cm⁻².

The Co-based catalysts have been explored for HMFOR.^[154-160] For instance, cobalt spinel oxides (e.g., Co₃O₄) with two kinds of Co geometric configurations have been applied for selective HMFOR into FDCA *via* a HMFCA pathway.^[157] This Co₃O₄ showed outstanding activity for HMFOR due to the involvement of both tetrahedral (Co²⁺_{Td}) and octahedral sites (Co³⁺_{Oh}) during HMFOR. Specifically, Co²⁺_{Td} provided more Lewis acidic sites to enhance the adsorption of electron-rich oxygen in carbonyl group, while Co³⁺_{Oh} appeared to be active site to oxidize HMF. When Co²⁺ is further replaced by Cu²⁺, stronger Lewis acidic sites in CuCo₂O₄ was obtained to promote HMFOR, thus only required a low potential of 1.37 V vs. RHE to deliver a high current density of 150 mA cm⁻². Similarly, single Ir atom loaded spinel oxide Co₃O₄ (Ir-Co₃O₄) catalyst has been applied for HMFOR *via* a HMFCA pathway.^[156] The

introduction of single Ir atoms is believed to enhance the adsorption for C=C groups and hence this catalyst exhibited a decreased onset potential(1.15 V vs. RHE) compared to Co₃O₄ (1.35 V vs. RHE). The role of oxidation states of Co-based materials (Co³⁺ and Co⁴⁺) toward HMFOR has been studied,^[158] where Co³⁺ was assumed to oxidize HMF to HMFCA and no further oxidation of hydroxyl group occurred at an applied potential of 1.1 V vs. RHE. Once the applied potential increased, oxidation of partial Co³⁺ into Co⁴⁺ happened. The Co⁴⁺ species effectively oxidized hydroxyl and formyl groups, leading to the FDCA formation. This process is different from the HMFOR mechanism on Ni-based catalysts where Ni³⁺ species is the active site and no selectivity is noticed for the oxidation of hydroxyl and formyl groups. Besides, heterogeneous interface (such as CuO-PdO^[161]) and main group pblock metal peroxide (such as InOOH^[162]) were constructed to boost HMFOR through enhancing the adsorption of HMF and OH⁺.

In addition to intrinsic activity of catalyst, selectivity of products was determined by applied potential and pH of electrolyte. Different applied potential results in different valence status of an active metal, thus the reaction pathway was changed accordingly. [158, 163-164] In a typical case of nano-Cu catalysts, HMFCA and H₂ as the main product was detected when the potential was applied below 0.4 V vs. RHE (Figure 9e) at a pH value of 14, then FDCA acted as the main product as the applied potential increased (Figure 9f).^[163] Meanwhile, when H₂ was produced via the rection from HMFOR to HMFCA at low applied potential, the critical gem-diol intermediate 5-(Dihydroxymenthyl)furan-2-methanol (DHMFM) was captured by in situ Raman, in situ ATR-FTIR and isotope tracking.^[164] DHMFM reacted with OH⁻ to generate gem-diolate ion intermediate (DHMFM), then form gem-diolate dianion intermediate (DHMFM²⁻) by Cannizzaro reaction in 1 M KOH. Under low applied potentials (0.13-0.43 V vs. RHE), DHMFM²⁻ adsorbed on Au-Ni catalyst via Au-O binding was oxidized to HMFCA accompanied negatived charge H transfer to form Au-H bond and H₂. While under high applied potentials (0.53-0.93 V vs. RHE), a large number of DHMFM was oxidized to HMFCA meanwhile positive charge H transfer to react with OH⁻ for H₂O production. Besides, pH value also plays an important role in selectivity of product, since oxidation of aldehyde group is actively occurred in stronger media while oxidation of alcohol group prefers in weak alkaline and neutral electrolyte. For instance, the selectivity of products on a NiO₂H_x catalyst was investigated in different alkaline electrolyte (pH value from 9-13).^[165] Under weak

alkaline media (pH \leq 11), direct oxidation of alcohol group of HMF to produce DFF was preferential. When pH value was increased to11, the surface state of NiO₂H_x was changed from NiOOH to Ni(OH)₂, and DFF was still the main production due to the equal OH and O active sites. Then increasing the pH value to 13, NiOOH gradually transformed to NiO₂, aldehyde group was preferentially oxidized to generate FDCA. Additionally, a single-atom Ru loaded on NiO (Ru₁-NiO) exhibited the selectivity of 90% for DFF generation at pH value of about 7. It was confirmed OH* is active site rather than Ni³⁺ for DFF generation. In neutral media the incorporation of Ru atoms restricted the formation of Ni³⁺ and promoted the OH* generation.^[166]

Aldehyde oxidation reaction of furfural (FUROR) has been also wildly discussed in recent years.^[11, 167-172] Furfural acid is a primary product for FUROR, which is often used in plastic, food and medicine fields.^[171] In this regard, a Cu/Cu foam catalyst exhibited an excellent activity for FUROR occurred at a potential of about 0 V vs. RHE, and the generation of furfural acid was realized.^[11] Additionally, electrooxidation of formaldehyde from industrial wastewater (e.g., plastic, synthetic fibers, dyeing and medical industry) to form valuable formate also have been investigated recently.^[38, 173-174] In this aspect, Cu₃Ag₇ alloy exhibited the lowest onset potential of -0.01 V vs. RHE, superior to CuAg with other mole ratio and single Ag or Cu.^[38] However, the over oxidation of HCHO to form CO₂ would be occurred if current density exceeds 60 mA cm⁻². Furthermore, paraformaldehyde alternative to HCHO would exhibit enhanced activity, only required a potential of 0.13 V vs. RHE



Figure 9. (a) Reaction pathway of HMFOR. (b) Concentration versus time plot. (c) Operando ATR-FTIR spectra at various applied potential after 20 min of applied potential. Reproduced with permission.^[147] Copyright 2018, Wiley-VCH. (d) Free energy profiles of HMFOR to FDCA on NiOOH catalyst. Reproduced with permission.^[152] Copyright 2021, Wiley-VCH. Product concentration versus applied potential (e) for the low-potential oxidation, (f) high-potential oxidation. Reproduced with permission.^[163] Copyright 2022, Nature. (g) LSV curves with iR-correct in 1 M NaOH with and without 1 M Na₂S. (h) HRTEM image of WS₂ nanosheets. Reproduced with permission.^[175] Copyright 2021, Wiley-VCH. (i) Adsorption capacity of adsorption rate of S²⁻ for CoS₂@C/MXene/NF and CoS₂@C/NF. Reproduced with permission.^[176] Copyright 2022, Wiley-VCH.

3.2.5 Sulfion oxidation reaction

Sulfion oxidation reaction (SOR) attracts attentions due to its lower theoretical potential of -0.48 V ($S^{2-} \rightarrow S + 2e^{-}$) to obtain valuable S ^[35] and removing toxicity in wastewater. Several transition metal oxide^[177-178] and sulfide^[175-176, 179-182] have been reported for SOR in recent years. For example, WS₂ nanosheets synthesized through a molten-salt-assisted method have been applied as a catalyst for SOR.^[175] This catalyst exhibited a low potential of 0.48 V vs. RHE at a current density of 10 mA cm⁻² in 1 M NaOH (**Figure 9g**), thanks to its rich edge sites (**Figure 9h**). However, the product S was deposited on the catalyst surface to hinder further reaction. In another case, the strong and spontaneous adsorption of S²⁻ and polysulfides (S_2^{2-} , S_3^{2-} , S_4^{-} , S_8^{2-}) have been verified on Co₃S₄ nanowires.^[182] Therefore, the energy barriers of RDS (S₃²⁻ to S₄⁻) and desorption of S_8 were obviously decreased revealed by DFT calculations. In order to reduce accumulation rate of S_8 , a $CoS_2@C/MXene/NF$ with exposed active phase $CoS_2(111)$ in the microporous MXene/NF, the large surface area, and the enhanced S^2 -adsorption capacity was designed to boost SOR.^[176] This catalyst exhibited a superior performance due to lower energy barriers of RDS (S_2^* to S_3^*) and weak affinity of S avoiding the S deposition (**Figure 9i**).

In a short, electrochemical synthesis reactions would provide value-added chemicals determined by the suitable electrocatalysts. These reactions based on small molecules with long carbon chains or multiple functional groups (e.g., -OH and - CHO) generally undergo complex pathway resulting in a low selectivity, which is the biggest challenge at present. A variety of factors could be applied to enhance the selectivity including active sites, pH of electrolyte, interface microenvironment, and so on.

Catalysts	Electrolyte	E_{ESRs} (V vs.	Coupled	V _{cell} (V@mA	Ref.		
	(Substrate + 1.0	RHE @mA	electrolyzer	cm ⁻²)			
	M KOH)	cm ⁻²)					
$Ni_{0.75}Fe_{0.25}Se_2$	1.0 M methanol	1.5@53.5			[113]		
CNFs@NiSe	1.0 M methanol	1.43@100			[183]		
NiP _x -R	0.5 M methanol	1.40@400			[110]		
NiS NPs	1.0 M methanol	1.368@10			[184]		
mSnO ₂ /CC	1.0 M methanol	1.47@100			[27]		
NiO/NF	1.0 M methanol	1.53@100			[87]		
h-NiSe/CNTs	1.0 M methanol	1.52@100			[114]		
Co(OH)2@HOS/CP	3.0 M methanol	1.385@10	MOR HER	1.497@10	[185]		
NiFe ₂ O ₄ /NF	0.5 M methanol	1.43@100	MOR HER	1.74@100	[186]		
Ni _x Co _{1-x} (OH) ₂	0.5 M methanol	1.33@10	MOR HER	1.5@10	[187]		
Ni(OH) ₂ /NF	0.5 M methanol	1.36@100	MOR HER	1.62@50	[112]		
Nilr-MOF/NF	4.0 M methanol	1.41@100	MOR HER	1.39@10	[188]		
mSnO ₂	1.0 M methanol	1.47@100	$MOR \ CO_2 RR$	0.93@10	[27]		
Ni-NF-Af	0.5 M methanol	1.345@100	MOR CO ₂ RR	2.13@10	[40]		
Co _x P@NiCo-LDH	0.5 M methanol	1.34@100	MOR HER	1.43@10	[189]		

 Table 3. Performance of recently reported electrocatalysts for ESRs and related coupled electrolyzers.

Co(OH) ₂ @Ni(OH) ₂	1.0 M ethanol	1.301@10	EOR HER	1.464@100	[122]
SA In-Pt NWs/C	0.5 M ethanol		EOR HER	0.62@10	[118]
NiOOH-CuO	1.0 M ethanol	1.347@200	EOR HER	1.43@50	[123]
PtCu nanoframe	0.5 M ethanol	0.50@10	EOR HER	0.58@10	[119]
PdAg/NF	1.0 M ethylene	0.57@10			[124]
	glycol (in 0.5 M				
	KOH)				
Au/CoOOH	0.1 M benzyl	1.5@540			[135]
	alcohol				
BdIr BNRs	1.0 M			0.38@10	[137]
	isopropanol				
Ni-Mo-N/CFC	0.1 M glycerol	1.3@10		1.36@10	[29]
MoO _x /Pt	0.1 M glycerol		GOR HER	0.70@10	[125]
RhCu-ultrathin	0.1 M glycerol	0.53 (onset)	GOR NRR	0.9@10	[190]
nanoflake	(in 0.1 M KOH)				
InOOH-O _v	0.05 M HMF	1.34@10	$HMFOR \ CO_2$	2.27@10	[162]
			RR		
Ru(III)-PEI@MWCNT	0.001 M HMF		HMFOR NRR	1.34@0.5	[15]
FeP-NiMoP ₂ /FeNi	0.01 M HMF	1.366@100	HMFOR 4-	1.13@10	[17]
foam			NBA ERR		
$CuCo_2O_4$	0.05 M HMF	1.23 (onset)			[157]
Ni _x B	0.01 M HMF	1.45@100			[147]
Metallic Cu	0.1 M HMF		HMFOR HER	0.27@100	[163]
Metallic Cu	0.2 M furfural		FUROR HER	0.31@100	[163]
Cu/Cu foam	0.05 M furfural	0 (onset)			[11]
Cu_3Ag_7	0.6 M	0.4@66	FOR HER	0.13@100	[173]
	formaldehyde				
NiFeO _x -NF	0.05 M glucose	1.3@87.6			[32]
Mn-a-Ni(OH) ₂	0.025 M benzyl	1.31 (onset)			[107]
	amine				
NiSe nanorod	0.001 M benzyl	1.35 (onset)			[103]
	amine				
Co_3S_4	$1.0 \text{ M Na}_2\text{S}$	0.262@100			[182]

4. Coupled electrolyzers

4.1 Coupled HER with oxidation reactions of small molecules

Coupling small molecule oxidation reactions with HER is a promising way to boost H_2 production. Compared to a conventional OWS system which consists of anodic OER and cathodic HER (OER|HER), this new coupled electrolyzer system has its unique features. Firstly, a lower cell voltage than that of an OWS system is possible for this coupled electrolyzer system, mainly due to the lower theoretical potential of SAORs than OER. Secondly, this system can avoid explosion dangerous derived from the mixture of H_2 and O_2 , and membrane degradation due to the lack of reactive oxygen species. Last but not least, this system can recycle wastewater (containing urea, hydrazine or ammonia) and provide value-added products (e.g., formate, glycerate, FDCA, etc.).

4.1.1 Coupled HER with SAORs

One typical of this coupled system is the composition of UOR and HER, which delivers lower cell voltage than an OWS system for H₂ production, accompanying with urea deleting. Note that HER is usually not affected by urea in electrolyte. Some studies even stated that urea presence is beneficial for the HER.^[62, 64] Thus, membrane is unnecessary for UOR HER electrolyzer. In addition, transition metal-based catalysts have been applied to replaced commercial Pt/C catalyst for this coupled electrolyzer. To obtain enhanced performance of coupled system, bifunction catalysts are the first option. One strategy to construct bifunctional catalysts is combining two cathodic and anodic reaction active species. For example, a UOR HER was constructed applied CoS₂-MoS₂ as a bi-catalyst. This device exhibited a voltage of 1.29 V at a current density of 10 mA cm⁻², proceeding 60 h at this current density without degradation, surpassed a standard OER HER (1.45 V).^[65] Another strategy is designing suitable heterostructure. For instance, a Ni/W₅N₄/NF heterostructure severed as a bi-catalyst for facilitating UOR HER system (Figure 10a). This device only required a low voltage of 1.77 V to drive an industrial-scale large current density of 1000 mA cm⁻² (Figure 10b), and could maintain the current density of 100 mA cm⁻² for 100 h without obvious current change (Figure 10c).^[72] Similar to a UOR HER system, a HzOR HER system has been proposed using Ni-Co-P/NF as a bifunctional catalyst. The coupled system required a voltage of 0.88 V to reach a current of 200 mA cm⁻², and exhibited a strong stability during continuous operation remained at 100

mA cm⁻² for 30 h.^[85] Another HzOR HER electrolyzer was constructed using bifunctional Ni-C HNSA catalyst, which exhibited a more desirable cell voltage of 0.4 V to deliver a current of 200 mA cm⁻² (**Figure 10d**), much lower than an OER HER system (**Figure 10e**).^[79]

4.1.2 Coupled HER with ESRs

In addition, ESRs has been integrated with HER. Such a coupled system is a meaningful routine because the value-added products can be obtained from these oxidation reactions in addition to H₂ production. MOR HER electrolyzer is one of coupled HER with ESRs. For example, a MOR HER system using NiIr-MOF/NF as a bifunctional catalyst exhibited a cell voltage of 1.39 V at a current density of 10 mA cm⁻² (Figure 10f), obviously lower than that in OWS system (Figure 10g). Meanwhile, the value-added formate was produced.^[188] Moreover, a MOR HER system operated in seawater instead of pure water has been presented using a $NiFe_2O_4/NF$ as a bifunctional catalyst, which can avoid the interference from chlorine oxidation reaction.^[186] This system exhibited a cell voltage of 1.74 V to deliver a current of 100 mAcm⁻², than OER HER electrolyzer (1.89 V). Meanwhile, the MOR HER electrolyzer maintain the current density of nearly 700 mA cm⁻² for 6 h in seawater. To improve the value for practical application, even in industrial application, larger current density meaning high concentration of electrolyte and stable operation for a long time are prerequisites but a grand challenge for these coupled HER with ESRs. Fortunately, a BOR||HER system reached the standard of industrial application, where applied electrolyte was 3 M KOH with 0.2 M benzyl alcohol, meanwhile a flow electrolyzer process without membrane was used.^[135] This device exhibited a high benzyl alcohol conversion rate of 39.8 mmol h⁻¹ and a high yield of H_2 of 1.9 L h⁻¹.

Compared alcohol oxidation reactions, aldehyde oxidation reactions exhibit lower theoretical potential, thus resulting in a wonderful performance of coupled ESRs with HER systems at low energy consumption. In addition, the oxidation of aldehydes would produce valuable acids and H₂, forming a so-called bipolar hydrogen production system. For example, in HMFOR HER and FUROR HER systems,^[163] HMF and furfural were oxidized to HMFCA and 2-furoic acid, respectively, accompanying with H₂ generation at the anode, coupled with cathodic HER (**Figure 10h**). A cell voltage of 0.27 V and 0.31 V were required to deliver a current of 100 mA cm⁻² for HMFOR HER (**Figure 10i**) and FUROR HER (**Figure 10j**), respectively. As a result, the electric energy consumption for H_2 production was decreased to around 0.35 KWh per m³ H_2 in this bipolar hydrogen production system, obviously better than 5 KWh per m³ H_2 for OWS system. The same situation were also occurred in FOR HER electrolyzer using paraformal dehyde as anodic substrate^[173]. To further reduce energy consumption, using solar cell to drive these coupled electrolyzers becomes a new strategy. For example, an ultra-low electricity consumption for H_2 generation (2.32 KWh per m³ H_2) has been realized in a 1 W solar-driven SOR HER electrolyzer, accompanying with value-added S production.^[176]



Figure 10. (a) LSV curves of the Ni/W₃N₄/NF catalyst, with the inset showing an illustrative schematic of urea-assisted water electrolysis system. (b) LSV curves of Ni/W₃N₄/NF catalyst in HER^{II}UOR and HER^{II}OER coupling systems. (c) The two-step chronopotentiometric (CP) curve of HER^{II}UOR coupling system. Reproduced with permission.^[72] Copyright 2022, Elsevier. (d) LSV curves, (e) Comparison of cell voltage at different current density for OHzS and OWS. Reproduced with permission.^[79] Copyright 2022, Wiley-VCH. (f) Schematic illustration, (g) LSV curves for NiIr-MOF/NF^{II}NiIr-MOF/NF system. Reproduced with permission.^[188] Copyright 2022, Elsevier. (h) Schematic for anodic low-potential aldehyde oxidation and cathodic HER. (i) LSV curves of HMFOR, (j) LSV curves of FUROR using Cu foam as the anode and Pt/C as the cathode. Reproduced with permission.^[163] Copyright 2022, Nature.

4.2 Coupled ORR with oxidation reactions of small molecules

Oxidation reactions of small molecules have been coupled with oxygen reduction

reaction to construct fuel cells. For example, a system integrated FUROR with ORR

(shown in Figure 11a) was used to generate valuable furoic acid and H_2 and output the electricity.^[11] Furoic acid and H_2 were simultaneously generated at the anode with a negative potential (nearly 0 V vs. RHE), ORR was occurred a positive potential, thus producing a fuel cell. Under optimum conditions, this device showed a peak power density of 200 mW cm⁻² with a H_2 yield of approximately 2 kWh per cubic meter of H_2 (Figure 11b). Similarly, a direct hydrazine fuel cells (DHzFCs) was designed to construct a self-powered H_2 generated system *via* combining anodic HzOR and cathodic ORR (Figure 11c).^[12] The formed DHzFCs demonstrated a maximum power density of 46.3 mW cm⁻² to drive H_2 production, accompanying a competitive rate of 1.25 mmol h⁻¹ for H_2 generation at room temperature.

In some special circumstances, ORR can be coupled with oxidation reactions of small molecules to produce H_2O_2 at low energy consumption, which has wide application such as wastewater treatment, paper bleaching, chemical synthesis.^[52, 191-192] Different from fuel cells, such systems mainly aim at the generation of value-added chemicals or pollutant removing, rather than outputing the electricity. In this regard, a UORI2e ORR system was constructed,^[52] which exhibited a high H_2O_2 generation rate of 225.3 gm⁻²h⁻¹ with a faradaic efficiency of 82.3 % as well as a urea elimination rate of 140.1 gm⁻²h⁻¹ with a faradaic efficiency of 94.9 % at a low voltage of 0.63 V. This coupled system can be further optimized to meet the economic demand, as illustrated by a GORI2e⁻ ORR electrolyzer, where glycerol were contained both at anode and cathode separated by a Nafion membrane. Interesting, the product H_2O_2 at the cathode would further transfer to \cdot OH *via* electro-Fenton process, then oxidize glycerol to the desirable C_3 oxidation products as same as that occurred in the anode (**Figure 11d**).^[191]



Figure 11. (a) Illustration of FUROR lORR coupling system. (b) Polarization and

power-density curves. Reproduced with permission.^[11] Copyright 2021, Wiley-VCH. (c) Schematic illustration of DHzFC driven HzOR HER system. Reproduced with permission.^[12] Copyright 2020, Nature. (d) Schematic illustration and working principle of GOR 2000 Permission.^[19] Copyright 2022, Nature.

4.3 Coupled CO₂RR with oxidation reactions of small molecules

Carbon dioxide reduction reaction (CO_2RR) is attractive in utilizing the greenhouse gas CO₂ as the feedstock to generate high value-added C₁ (CO, HCOOH, CH₃OH, CH₄), C₂ (C₂H₄, C₂H₅OH, C₂H₆, CH₃CHO, CH₃COOH) and C₂₊ (C₂H₅CHO, n-C₃H₇OH) chemicals. Due to sluggish kinetic of OER, huge energy consumption is thus required for CO₂RR integrated with OER.^[36, 39, 193] To tackle such an issue, OER has been replaced with oxidation reactions of small molecules, such as the construction of a SAORs||CO₂RR or ESRs||CO₂RR. As far as SAORs||CO₂RR is concerned, a UOR||CO₂RR system was constructed (**Figure 12a**),^[13] where Ni-WO_x and Ag nanoparticles severe as anodic and cathodic catalysts, respectively. Besides the advantage of removing pollutant, this system only required a cell voltage of 2.16 V to deliver a current of 100 mA cm⁻², 370 mV much lower than OER||CO₂RR, resulting in 15% less energy consumption (**Figure 12b**).

On the other hand, once ESRs CO₂RR electrolyzer systems are built, valuable chemicals are probably produced at both anode and cathode. In this regard, a coupled MOR CO₂RR can produce the valuable formate simultaneously at both anode and cathode.^[40] Meanwhile, a cell voltage of 2.13 V was only needed to reach a current of 10 mA cm⁻², lower than that of OER CO₂RR system (Figure 12c). Among the electrolyzers coupling CO₂RR and three oxidation reactions (namely OER, GOR and glucose oxidation),^[41] the GOR CO₂RR system demonstrated a lowest cell voltage of nearly 0.75 V with reduced electricity consumption (Figure 12d), accompanying with efficient formation of high-value products such as HCOO⁻, lactate, CO and HCOOH. This suggests the important role of selecting small molecules to match CO₂RR. It is also found the applied catalysts are also vital for this coupled CO₂RR system. For example, InOOH nanosheet with rich oxygen vacancies (InOOH-O_v) was used in CO₂RR HMFOR to generate valuable formate and FDCA.^[162] Due to the charge redistribution of InOOH induced by oxygen vacancies, the adsorption of $*CO_2$ was enhanced to accelerate formate production. The HMFOR CO₂RR electrolyzer exhibited an outstanding faraday efficiency of 92.6% for reducing CO₂ to formate and a FDCA yield of 91.6%. Up to date, CO and formate were main cathodic products for

SAORs $||CO_2RR|$ or ESRs $||CO_2RR|$ systems and their selectivity was relatively high. However, generation of C₂ and C₂₊ chemicals is still a challenge due to the sluggish kinetic of C-C band formation. Therefore, promoting CO₂ conversion to C₂ or C₂₊ products are vital for SAORs $||CO_2RR|$ and ESRs $||CO_2RR|$ systems in future.

4.4 Coupled NRR with oxidation reactions of small molecules

Direct reduction of N₂ into NH₃ or N₂ reduction reaction (NRR) is crucial because NH₃ is an important raw material applied in wide fields of fertilizer, medicine and fine chemicals.^[37, 194] Traditional method to synthesize NH₃ is so-called a Haber-Bosch approach, which occurs with aid of Fe-based catalysts under high pressure and high temperature. In 2021, the NH₃ yield of this approach has reached 182 million metric tons.^[194-195] However, this traditional method still faces serious problems such as extensive energy consumption and massive emission of CO₂. In this context, electrochemical NRR, namely electrochemical production of NH₃ from N₂ has been proposed as an alternative strategy to the Haber-Bosch approach. However, low FE (< 20%) and poor yield (µg level) of electrochemical NRR are existing obstacles mainly due to the fast HER heavily competes with NRR.[196-197] In this regard, designing advanced catalysts such as Sn-doped black phosphorene (Sn-BPene)[198] and MoB2 with $Mo^{\delta+}$ (0 < δ < 4)^[199], to improve the adsorption of N₂ while limit the adsorption of H₂O was wildly accepted as a promising strategy to facilitate the NRR. On the other hand, the pH of electrolyte also played an important role in the performance of NRR, whose activity followed the order: 0.1 M Na₂SO₄ > 0.1 M KOH > 0.05 M H₂SO₄.^[199] Objectively speaking, the efficiency of electrochemical NRR is far below the standard of industrial application. Therefore, NRR coupled with oxidation reactions of small molecules is rarely reported up to date. In the case of HMFORINRR coupled electrolyzer using Ru() polyethyleneimine on carboxyl-modified carbon nanotubes (Ru()-PEI@MWCNTs) as a bifunctional catalyst,^[15] an enhanced NH₃ yield of 188.9 $\mu g_{NH3} m g_{cat}^{-1} h^{-1}$ with a faradaic efficiency of 30.39% was achieved compared to Ru()@MWCNTs, PEI@MWCNTs and MWCNTs (Figure 12e). In another case, a GOR INRR coupled system exhibited a high NH₃ yield of 92.01 µg_{NH3}mg_{cat}⁻¹h⁻¹ which remained well even during continuous operation for 12 h.[190]



Figure 12. (a) Schematic image, (b) LSV curves of the UOR CO₂RR electrolyzer. Reproduced with permission.^[13] Copyright 2021, Wiley-VCH. (c) LSV curves of UOR CO₂RR electrolyzer. Reproduced with permission.^[40] Copyright 2021, Wiley-VCH. (d) Electrochemical performance for CO₂RR to CO on silver, coupled to OER, glycerol and glucose electrooxidation at the anode. j_{CO} as the function of the cell potential. Reproduced with permission.^[41] Copyright 2019, Nature. (e) LSV curves of Ru()-PEI@MWCNTs for NRR coupled with OER and HMFOR. Reproduced with permission.^[15] Copyright 2019, The Royal Society of Chemistry. (f) Schematic illustration of FOR NO₃-RR system. (g) Schematic image of flow electrolyzer. Reproduced with GDE. (i) Schematic image of MEA electrolyzer. Reproduced with permission.^[147] Copyright 2018, Wiley-VCH. (h) Schematic image of flow electrolyzer. Reproduced with generation of MEA electrolyzer. Reproduced with permission.^[147] Copyright 2018, Wiley-VCH. (h) Schematic image of flow electrolyzer. Reproduced with generation of MEA electrolyzer. Reproduced with permission.^[147] Copyright 2023, American Chemical society.

4.5 Other coupled electrolyzers based small molecules

Some organic reduction reactions including electroreduction of R-NO₂ to R-NH₂ also have been applied in coupled electrolyzers.^[17, 201] For example, cathodic reduction of 4-nitroenzyl alcohol coupled with HMFOR was constructed to produce the valuable FDCA and 4-aminobenzyl alcohol at low energy consumption.^[17] Similarly, the reduction of 4-nitrophenol (4-NP) was coupled with HMFOR exhibited the excellent FE and yield (FE of 98.75 and yield of 95.55 for reduction of 4-NP, FE of 99.8% and yield of 96.45% for HMFOR), which not only removed a pollutant in wastewater, but also obtained valuable 4-aminophenol (4-AP).^[202] In some specific

condition, coupled the oxidation and reduction of the same small molecules such as aldehyde was reported. For example, the reduction of HMF occurred in 0.2 M HClO₄ was coupled with the oxidation of HMF in 1 M KOH, where a bipolar membrane was needed.^[18] In this means, the more valuable FDCA and DHMTHF were obtained with the high conversion of 92% and 87%, respectively.

Besides, formaldehyde oxidation was coupled with NO₃ reduction reaction (NO₃ + $6H_2O$ + $8e^- \rightarrow NH_3$ + $9OH^-$) in a flow electrolyzer with a proton exchange membrane.^[38] This device can remove pollutants of HCOOH and NO₃⁻, simultaneously generate the valuable formate and NH₃, meanwhile output electricity of 102 kWh per ton ammonia generation, obviously lower the traditional electricity consumption (Figure 12f). Note that the large overpotential, complex pathways and toxic intermediate (e.g., NO₂, NO, NH₂OH) for are also the existing main challenge for NO₃RR to NH₃.^[16] Importantly, selected reactions of small molecules for coupled electrolyzers are not arbitrarily. Their thermodynamic and kinetic matchings are the two key factors. Thermodynamically, a lower gap in theoretical potential for oxidation and reduction reactions of small molecules is more promising for a coupled system, maximizing the reduction of energy consumption. Kinetically, coupled electrolyzers can possess the best performance when the oxidation and reduction reactions are with an identical reaction rate. Especially for anodic oxidation reactions, their reaction rates are sensitive to applied potentials, stemming from their sluggish dynamics of multi-electron transfer. Such matching in thermodynamic and kinetic will offer new contribution for the evaluation of constructed coupled electrolyzers and finally industrial applications.^[17]

4.6 Construction of coupled electrolyzer

The configuration of coupled electrolyzers is worthy of consideration, which is particularly desirable for scaling up coupled electrolyzers from a laboratory scale to industrial level. The simplest configuration for coupled electrolyzers was fabricated in in one chamber without membrane. Up to now, SAORs, MOR and EOR coupled with HER electrolyzers were always evaluated in one chamber electrolyzer without any membrane. The performance of cathodic HER was not affected by urea for anodic UOR.^[72] And the products of SAORs were N₂ and CO₂, which can avoid the risk of contact of H₂ and O₂ in OWS system. Thus, membrane can be omitted for SAORs||HER electrolyzer. Besides, in the case of selective MOR and EOR coupled with HER systems, membrane were also not applied, since anodic methanol, ethanol

and their products formate could not influence HER on the designed transition metalbased catalysts.^[29, 186] However, limitations of performance are often occurred in this configuration, especially at a large current density, due to the possible interference of electrolyte and products. Some small molecules (e.g., glycerol, HMF, glucose and S²⁻) could be reduced at cathode to disturb cathodic reactions or influence the solution mass transfer.^[125] In order to avoid the interference for evaluating the performance, Htype electrolyzer with anion exchange membrane (AEM) or proton-exchange membrane (PEM) was employed. Most HMFOR, FUROR and SOR coupled with HER were constructed in H-type cell with Nafion membrane, other oxidation of alcohols (e.g., ethylene glycol, glycerol and benzyl alcohol) and glucose coupled with HER were also performed in this configuration but using AEM membrane. However, H-type electrolyzer is only suitable for laboratory-scale research due to the limited mass transfer and electrolyte volume. Thus, the flow electrolyzer for continuous operation have been performed (Figure 12g). It can shorten the distance of anode and cathode, decrease the ohmic loss, and thus improve the efficiency of mass transfer. In the case of gas as reactant, especially insoluble gas (e.g., CO₂ and N₂), addition of hydrophobic diffusion layer (GDL) (Figure 12h) can enhance the gas diffusion, ensure full contact between gas and catalyst and realize more large current density.^[203] Besides, carbon corrosion, overflow of electrolyte and gas channel was blocked by carbonate caused the poor stability. Furthermore, membrane electrode assembly (MEA) electrolyzer (Figure 12i) was constructed. The zero gap between catalysts and membrane was realized by catalysts coated substrate (CCS) and catalysts coated membrane (CCM), which can decrease the ohmic resistance and improve reaction efficiency. For example, when a MEA flow electrolyzer with AEM membrane was employed for EGOR || HER, the current density of 500 mA cm⁻² was realized only required 1.77 V vs. RHE.^[129] Until now, just few cases were performed in flow electrolyzer even MEA flow electrolyzer. The performance of coupled systems at industrial scale current density in flow electrolyzer is rarely reported, more efforts should be devoted to boosting the design of configurations of coupled electrolyzers.

Generally, PEM used in acid media while AEM in alkaline media. However, it still exists exceptional cases where PEM membrane such as Nafion 117 was used in KOH electrolyte toward HMFOR and FUROR based coupled electrolyzers for arriving at wonderful performance.^[148, 159, 162, 204] The Nafion 117 also was applied in SOR||HER system to ensure Na⁺ transport and maintain ion balance.^[182] Besides, when

the pH of an electrolyte is different at both anodic and cathodic zones, a bipolar membrane (BMP) is needed. However, the configuration of a BMP is complex, consisting a cation and anion membrane with an additional interface layer. Catalysts are anchored in interface layer to catalyze water dissociation and maintain the pH gradient.^[205] For example, this membrane was used MOR||CO₂RR electrolyzer to separate the andic KOH containing methanol and cathodic KHCO₃ media.^[40] Although PEM has shown the advantages in terms of the higher current density, catalytic efficiency and stability for coupled system, their high cost limited their industrial applications. In contrast, anion exchange membranes (AEMs) can be produced at relatively low costs, while their lower conductivity and terrible stability cause the poor efficiency for coupled systems, due to their polymer backbones and cation groups such as a quaternary ammonium group are easily attacked by OH⁻. For a BMP, relevant researches are still in the initial stage, many key issues such as swelling and layering of membrane, catalysts design of interface layer are expected to be resolved in future. No data demonstrates the performance of membrane was affected by small molecules, but its structure in alkaline media during long term operation. Thus, further efforts should be devoted to designing suitable polymer backbone and cation groups to enhance the stability of AEM^[206].

5. Conclusion and perspectives

Current advances in designing required catalysts for redox reactions based on small molecules have been summarized. Reaction mechanisms of some investigated SAORs and ESRs are discussed. Construction of electrolyzers coupled with SAORs/ESRs and HER or other reduction reactions (e.g., ORR, CO_2RR , NRR and other reduction reactions) is systematically examined. These coupled electrolyzers are explored to own huge potential in saving electrical energy, generating more highvalued chemicals and mitigation of CO_2 emission. However, such couple systems are still in initial and tremendous efforts are necessary. In the following part, challenges and chance of developing couple electrolyzers are discussed and outlined.

5.1 Selection of small molecules

Selecting a suitable small molecule is a key prerequisite. Ideal small molecules are better to have high solubility and easily obtained by industrial manufactures at low price. Exploration and development of more biomass-derived small molecules with low oxidation potential is a promising strategy to produce value-added chemicals or remove the pollutions in wastewater.

5.2 Electrocatalysts

The catalysts are the most determined part to construct coupled electrolyzers. Considering high cost and scarcity of noble metals despite their outstanding activity, they need to be replaced by non-noble metal-based catalysts. Transition metals, especially Ni-based catalysts are promising catalysts for oxidation of some small molecules (e.g., UOR, HzOR and MOR). On the other hand, transition metals-based catalysts do not work well for more complex oxidation reactions of small molecules. Tremendous efforts are indispensable to further investigate relationship between activity of a catalyst and its structure. Experimentally, moderating electronic structures and/or adsorption energy of reaction intermediates shall be carefully considered during catalyst design by use of doping, alloying, defects introduction, heterostructure and others. Theoretically, mathematical calculations or theoretical simulations need to conduct to further explore reaction mechanisms of these reactions and meanwhile offer predictions of different catalysts. Machine learning based on advanced high-throughput methodologies and big data will facilitate rapid and efficient screening of catalysts in these coupled electrolyzers, revealing their structure-activity relationships. Novel strategies of breaking or bypassing the scaling relations *via* molecular enhancement, nanoconfinement, high-entropy alloy approaches should be deeply considered in the future. Last not least, ex situ, in situ and operando technologies should be used to trace dynamic changes, investigate reaction pathways and define true active sites of catalysts for different oxidation reactions. Of specifical interest, change of electronic structures and coordination states of active species needs to be explored by in situ X-ray adsorption spectroscopy (XAS) and XPS, critical intermediate need to be traced by in situ Raman, ATR-FTIR and isotope. Another fact is that the stability of reported non-noble metal-based catalysts is often missing. In our opinion, unique nanostructures (e.g., nanotubes, nanofibers, nanosheets and MOF-derived structures) with large surface areas and various porosities need to be designed and synthesized on different supporter (e.g., Ni foam, Cu foam, carbon paper and carbon cloth). In this way, desirable and more active sites will be exposed and mass transfer is possible to be enhanced.

5.3 Coupled electrolyzers

In coupled electrolyzers, as-obtained products were generally soluble. The separation of these liquid organic products is nonnegligible, especially for the cases where C_{2+} molecules (e.g., polyethylene glycol, glycerol, glucose and HMF) are

formed. When multiple products are only gained with low selectivity, the difficulty of their separation is further increased and meanwhile the economic efficiency of electrolyzers is decreased. To satisfy the industrial applications, unique MEA flow electrolyzers need to be considered based on oxidation reactions of small molecules. It shortened diffusion distance can enhance mass transfer, circulate the substrates at high concentration and decrease the solution resistance.

Some operation conditions for coupled electrolyzers shall be optimized. For example, pH of electrolyte is a key factor for oxidation of small molecules. However, most reported catalysts are active only in alkaline media. Developing advanced catalysts for coupled electrolyzers in non-alkaline media is still challenging—Regulation the interface microenvironment is also a possible factor affected the performance of coupled electrolyzers. For example, decreasing the alkalinity of electrolyte could adjust the benzaldehyde production for benzyl alcohol oxidation.^[136] Increasing the concentration of K⁺ could inhibit the competitive HER to improve the FE of NRR.^[207]

The applications of coupled electrolyzers in seawater should take more attention in order to save the cost of desalination and meanwhile purify seawater. However, the strong corrosion in electrolyzers inevitably occurs, due to complicated components of seawater and serious side-reaction of chloride evolution reaction on anode. To promote the development of coupled electrolyzers, a novel self-driven seawater purification electrolyzer can be assembled with self-breathable waterproof membrane and self-dampening electrolyte.^[208] Furthermore, construction of self-powered electrolyzer *via* coupling with oxidation reactions of small molecules and cathodic 4e⁻ ORR is an important way to realize higher electric energy input to output. Further integration of the self-powered device with coupled electrolyzer will be a novel and meaningful technology to simultaneously obtain value-added products and electric energy output. Other energy sources (e.g., solar cells) need to drive coupled electrolyzers. These profitable tactics can be for sustainable operation at low cost with low energy consumption.

In summary, although more efforts are required, coupling oxidation reactions of small molecules with reduction reactions, namely the formation of couple electrolyzers is a promising and energy-efficient approach to realize power to molecules and to remove environmental pollutants, eventually achieving sustainable development of our earth.

Competing financial interests

The authors declare no competing financial interests.

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Construction and progress of small molecule-based coupled electrolyzers

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This review summarizes state-of-art of coupled electrolyzers, the integration of oxidation reactions of small molecules (including sacrificial agent oxidation reaction (SAORs) and electrochemical synthesis reaction (ESRs) with reduction reactions including hydrogen evolution reaction (HER), oxygen reduction reaction (ORR), CO₂ reduction reaction (CO₂RR) and N₂ reduction reaction (NRR). Current challenges and prospects of this appealing strategy have been discussed and outlined.