Electrocatalytic Valorisation of Biomass Derived Chemicals

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ARTICLE

Electrocatalytic Valorisation of Biomass Derived Chemicals

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Electrocatalytic conversion of biomass-derived platform chemicals to value-added products can provide an approach to store large scale renewable energy (wind, solar) in chemical bonds. Recently, tremendous efforts have been made in this field. Herein, we discuss some general design principles of electrochemical devices for the conversion of biomass-derived intermediates. We primarily focus on the review of electro-valorisation of glycerol and also summarize the most recent advances in electrochemical conversion of 5-hydroxymethyl-2-furfural (HMF) through oxidation. We emphasize the role of both precious and non-precious metal electrocatalysts in electrocatalytic conversion in various practical electrochemical reactors and how to avoid competing reactions such as hydrogen evolution. We also provide a perspective on future opportunities and challenges in this field, including catalytic materials discovery, mechanism understanding, and system design.

1. Introduction

Biomass is an abundant and renewable hydrocarbon resource, which, however, has not been well utilized. Due to the increasing demand for sustainable energy and zero CO_2 emission etc., biomass conversion has become a popular research topic in the last decades.[1-4] Biomass-derived intermediates are potential key raw materials for chemical and energy sources.[2,5-9] One of the largest biomass products all over the world is lignocellulose that consists of 40-50 wt % of cellulose.[6] Cellulose can be further hydrolysed into C5 and C6 sugars.[7,10-12] Using biological or thermochemical processes, these sugars can be readily converted into platform molecules such as alcohols, glycerol, furans, levulinic acid, 5-hydroxymethyl-2-furfural (HMF),[11,13] which can be further valorised to value-added products.

The widely-used valorisation strategy for biomass-derived chemicals is the traditional thermal catalytic processes, which are commonly performed under relatively high temperatures (e.g., 200-300 °C), and sometimes consumes a large amount of hydrogen (i.e., in hydrodeoxygenation). Such operating conditions present great challenges in minimizing side reactions of reactive intermediates, maintaining hydrothermal stability of catalysts that are employed in condensed phase to accommodate wet nature of biomass feedstocks, and realizing sustainability, etc.[2] In contrast, electrocatalytic conversion using nanocatalysts has shown unique advantages. First, the electrocatalysis can proceed at low temperatures (typically less than 100 °C) and ambient pressure. More importantly, hydrogen is directly extracted from water and/or electrolyte solutions if needed (no additional hydrogen source is needed).[14,15] Second, electrochemical systems usually use module design which can be linearly scaled up or scaled down.[16] Third, the electrochemical reactions are sensitive to the electric double-layer, which can be tuned by the properties of electrocatalysts, applied potentials and electrolytes etc. Thus, the selectivity of products is expected to be facilely controlled by electrochemical parameters.

Electrochemical conversions are usually carried out in fuel cells and electrolysers (detailed devices and systems will be discussed in the following parts). The coupled electrochemical reactions must be considered during the design of device integrations towards a certain electro-valorisation reaction. For example, the water oxidation, i.e. oxygen evolution reaction (OER), is generally coupled with electro-reduction of biomass derived intermediates[17] and other reduction reactions such as hydrogen evolution reaction (HER),[18-20] electro-reduction of CO_2,[21] or nitrogen reduction to ammonia.[22-25] However, the coupled OER is pretty sluggish due to a large overpotential of over 0.3 V,[18,26,27] leading to low efficiency of whole devices. Accordingly, electro-oxidation of platform chemicals provides a highly valuable and efficient anodic process (up to almost 100 % selectivity in some cases, will be discussed below) to replace the inefficient OER. On the other hand, the competitive electrochemical reactions should also be considered, especially the possible competition of HER and electro-reduction of biomass-derived intermediates.

For the past several years, considerable efforts have been made on studying electro-valorisation of biomass-derived intermediates.[17,28,29] Among hundreds of biomass-derived intermediates,[11,12] electro-valorisation of glycerol and 5-

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hydroxymethyl-2-furfural (HMF) has been investigated intensively. Glycerol is a representative polyol and one of the most yielded products from biomass, with an annual world production of about several millions of tonnes.[11,30,31] HMF, another important building block with furan rings, −C=O and −OH groups all in its molecular structure,[17] provides a good model system for investigating biomass upgrading.

Some good review papers regarding electro-valorisation of glycerol[28] and HMF[17] have been published in the past few years. The previous review on glycerol mainly discussed the dependence of glycerol conversion on composition and structure of precious electrocatalysts.[28] Here we focus on recent progress in the past five years, particularly researches using practical devices. On the other hand, the recent HMF review included both reduction and oxidation of HMF, with a focus on HMF conversions, but lacked the discussions on possible competition between HMF reduction and HER,[17] which is included here. For further insights to these electro-valorisations for practical applications, better understanding on both the nature of electrocatalysts and the relationships between these electro-valorisations and competing HER in aqueous media is required. Herein, we summarize some general principles for electrochemical device design and review recent advances in this field with a focus on the correlation between nature of electrocatalysts, electrocatalysis conditions, and activity/selectivity in practical electrocatalytic reactors. We also pay attention to possible water redox reactions during the conversions (i.e., HER is a possible competing reaction for electro-reduction of biomass-derived intermediates) and provide some promising approaches to suppress the competitions.

2. Electro-valorisation devices and systems

Electro-valorisation processes include electro-oxidation and electro-reduction reactions, which are usually performed in aqueous acidic or alkaline electrolytes. The schematic illustration of typical devices for alkaline electro-valorisation is shown in Figure 1 and used as an example to briefly discuss the suitability of these devices as followings.

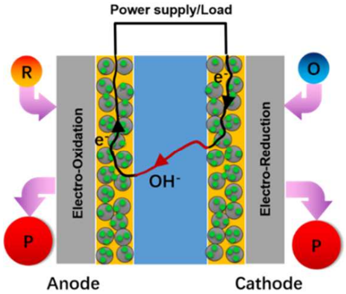

Figure 1. Schematic illustration of electro-valorisation devices including electrolyzers and fuel cells in alkaline electrolytes. R, O and P represent reductants, oxidants and products, respectively. Illustrations in acidic media and any other possible exhausted chemicals are omitted.

In an electrolytic cell, the electric energy is supplied to drive electro-oxidation reactions of biomass-derived intermediates and hydrogen production (hydrogen evolution reaction, HER) at anodes and cathodes, respectively (Figure 1). As a feasible alternative, HER can be replaced by electro-reduction of biomass-derived intermediates (will be discussed in the following part). Alternatively, electro-oxidation of biomass-derived intermediates (at lower potential range than the applied potential of oxygen reduction, i.e. < 0.9 *vs*. RHE,[32] reversible hydrogen electrode) can be coupled with oxygen reduction reaction (ORR) to build so-called cogeneration fuel cells,[28,33] which produce both electric energy and useful oxygenates such as aldehydes and carboxylic acids by feeding polyols such as glycerol at anodes (Figure 1). However, so far, the progress on cogeneration fuel cells has been slow because most electro-oxidation reactions of biomass derived intermediates require potentials higher than 0.9 V and the output voltages of such cogeneration fuel cells are very low which makes it much less attractive.[34,35]

Electro-reduction reactions of biomass derived intermediates include hydrogenation (or hydrodeoxygenation) or hydrogenolysis of polyols, alcohols, aldehydes, ketones and carboxyls etc. These reactions typically consume electric energy and form products at cathodes in an electrolyser instead of a fuel cell (Figure 1). Such electro-reduction reactions are commonly coupled with oxygen evolution reactions (OER). However, OER itself has many challenges like slow kinetics and low efficiency.[18,36,37] Thus, electro-oxidation of biomass-derived chemicals has been studied to replace OER[38,39] in such a configuration due to its lower overpotential than OER and its additional economic benefits by producing potentially value-added oxygenates products. Such integrations may potentially provide value-added products at both sides, and store electric energy in chemical bonds.[17] It should be pointed out that HER is a major competing reaction for electro-reduction of biomass-derived chemicals at cathodes. A currently feasible strategy is to employ catalysts with medium/high HER overpotentials (especially non-PGM metals) such as Fe, Ni, Cu, Ag, Pb etc. metals that suppress HER.

Based on the above discussions, when considering suitable devices (fuel cells *vs.* electrolytic cells) for electro-valorisation in aqueous solutions, the electrochemical reactions of oxygen and hydrogen (ORR, OER and HER) must be considered. Further, the electro-valorisation of biomass-derived chemicals can also be extended to organic electrolytes (e.g., acetone,[16] ionic liquids[40,41] etc.) due to their possible wide electrochemical windows and ability to solubilize most organic compounds, which could be helpful in controlling product selectivity. Such variable integrations including both fuel cells and electrolysers with different anodic/cathodic reactions and electrolytes present good opportunities to develop new energy conversion and storage technologies that need further exploration.

As we discussed above, glycerol and 5-hydroxymethyl-2-furfural (HMF) conversions by electrochemical approaches have been investigated more intensively than other biomass-derived intermediates, which is probably due to unique properties of these two platform chemicals. Glycerol is a simple

C3 polyol that contains two C-C bonds and three C-OH bonds in one molecule. Through controllable valorisation, glycerol can be converted into value-added building blocks such as hydroxypyruvate, dihydroxyacetone, glycerate, glyceraldehyde, tartronate etc. Besides, glycerol includes C-OH bonds with different chemical properties, i.e. terminal *vs*. middle hydroxyls, which can be an ideal model molecule to investigate the selective conversion of polyols. The investigations on glycerol are of great practical significance since glycerol is one of the most yielded biomass-derived intermediates. On the other hand, HMF, another important building block with simple molecular structures including furan rings, −C=O and −OH groups, provides a promising model system for investigating the upgrading of ring compounds. Thus, the following discussions primarily focus on electro-valorisation of glycerol and HMF.

3. Electro-oxidation of glycerol

Glycerol is a main by-product of biodiesel production and its yield has increased rapidly for the past several years.[30,42] Although the crude glycerol can be directly burned for generating heat, this application is less attractive due to the low heating value.[28] Glycerol has also been studied as a fuel for fuel cells,[43-55] but it might not be the most efficient way of utilizing glycerol because of its sluggish kinetics and incomplete oxidation[56] compared with C1 molecules including methanol and formic acid, leading to uncompetitive output power density. Interestingly, the incomplete oxidation of glycerol commonly results in value-added chemicals. With the increased production and the decreased price,[11,30] upgrading of glycerol to value-added chemicals instead of being used as the anode feed in fuel cells is therefore attracting more and more attention.

Traditional thermal catalytic conversion of glycerol has been intensively investigated to produce lactic acid,[57] 1,2-propanediol,[58] 1,3-propanediol, acrolein,[31] hydrogen (glycerol reforming),[59-62] esterification products between glycerol and acetic acid[63] and ketalization products between glycerol and acetone.[64] However, the catalysts for thermal conversion still suffer from rapid deactivation due to the polymerization/coking reactions of both reactant and intermediates as well as low hydrothermal stability of catalysts. For example, the remarkable fading of Bi modified Pt catalyst was observed after running for 20 h at 80 °C in an aqueous glycerol solution although the introduction of second metal enhanced the durability.[65] Besides, the selectivity of traditional thermal catalysis is low in some cases. For example, the thermal catalytic selectivity on Bi modified Pt catalysts for the conversion from glycerol to dihydroxyacetone (middle hydroxyl oxidation product) is only 53%.[65] In contrast, there has been some promising results reported on electrocatalytic valorisation of glycerol:[66] optimized electrocatalytic oxidation of glycerol tends to more selectively form middle hydroxyl oxidation products (close to 100% selectivity) instead of terminal hydroxyl oxidation, i.e. higher selectivity to dihydroxyacetone.[67] These facts indicate that the electro-valorisation is promising to handle glycerol conversion in terms of selectivity and stability. It should be mentioned that products of glycerol electrooxidation including glycerate, tartronate, dihydroxyacetone and glycolate etc. are important additives for food, polymer, cosmetics or pharmaceutical industry. The selective formation of these value-added products needs to be further explored.

The hydroxyl groups in glycerol molecules can be selectively electro-oxidized to form aldehyde (R-CHO), ketone (R-CO-R’) and/or carboxyl (R-COOH) groups. Several value-added products such as hydroxypyruvate, glycerate, glyceraldehyde, tartronate, dihydroxyacetone etc. with different degree of oxidation (DOX) have been produced via glycerol electro-oxidation on precious metal catalysts such as Pt,[68-73] Au[74-81] and Pd.[68,82-86] Noteworthy, glycerol oxidation was recently reported to be coupled with ORR in cogeneration fuel cells[34,87] or with HER in electrolytic cell,[88,89] which provides a promising direction for electro-valorisation of glycerol in electrochemical reactors that concurrently generate electric energy or hydrogen.

A good review was published a few years ago regarding glycerol electro-oxidation.[28] Up to date, the research on glycerol conversion has been mainly focused on precious metal catalysts.[90-97] In this review, we include newly published results and use some typical examples to illustrate how precious metal catalysts influence the performances.

3.1 Pt based catalysts

Pt has been studied as anode catalyst for glycerol oxidation in a cogeneration fuel cell. Typically, supported Pt nanoparticles with a face-centre cubic structure (Figure 2a) and a mean size of 2-3 nm (Figure 2b) was employed in the glycerol electro-oxidation.[34] As shown in Figure 2c, Pt nanoparticles are uniformly dispersed on Cabot Vulcan XC-72R carbon black, and employed as anode catalyst in an alkaline cogeneration fuel cell.[34] In such a device, glycerate and tartronate are mainly produced at lower anode potential (below ~0.5 V). The best selectivity for glycerate is 49%, whereas the selectivity for tartronate is 50%.

As the pH of electrolyte increasing, the power density of the fuel cell increases, and the selectivity to C3 acetates (glycerate, tartronate and mesoxalate) also increases.[34] The enhanced power density could be attributed to the improved OH^- diffusion rate and increased OH_{ads} coverage on Pt surfaces. The selectivity to C3 acetates may be attributed to the promoted deprotonation/dehydrogenation of hydroxyls in glycerol and therefore alkoxy intermediates formation on Pt facets by the enhanced OH^- concentration/OH_{ads} coverage.[98] It is notable that both the oxalate (fully oxidized C2 product) and mesoxalate (fully oxidized C3 product) with higher DOX are produced at lower glycerol concentration, indicating that the deep electro-oxidation reaction occurred at low reactant concentration albeit the low selectivity.[34] In addition, it is well-known that the introduction of a secondary metal can generate synergetic effects and thus remarkably promotes the electro-oxidation of intermediates, the so-called bifunctional mechanism.[99,100] This has been demonstrated in other systems, for example, Ru in PtRu alloys promotes the generation of OH_{ads} species, which can accelerate the oxidation of the poisonous intermediate CO, leading to significantly enhanced activity of the alloy catalysts in methanol electro-oxidation reaction.[99,100] Such an activity enhancement is also found for glycerol oxidation reactions,[75,80,95] leading to the production of compounds with high DOX such as tartronate on Pt catalyst in the presence of Ru and Rh.[101] Even though, the selectivity to tartronate is still < 50% and formate is observed on PtRu/C catalysts.[88]

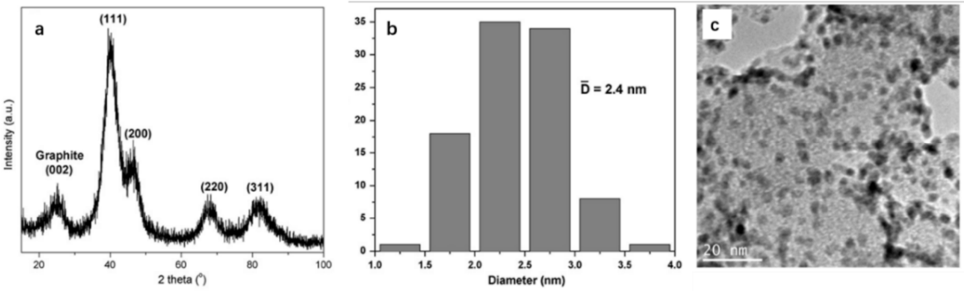

Figure 2. (a) XRD pattern, (b) particle size distribution, and (c) TEM image of Pt/C catalyst. The pictures are taken with permission from ref. 34. Copyright (2012) Elsevier B.V.

Based on the above discussions, chemicals with higher DOX are favoured at higher pH values and lower glycerol concentrations in alkaline media. In some cases where a secondary metal (e.g., PtRu, PtRh etc.) is used to facilitate the hydroxyl oxidation, deep oxidation of glycerol occurs. In addition, the secondary Ru metal in PtRu/C catalyst can also tune the binding energy of glycerol (optimal value is 1.75 eV when atomic ratio of Pt/Ru is 1:1), leading to higher glycerol oxidation activity.[102]

The selectivity to certain products thus far reported is still low,[34] e.g., the best selectivity to glycerate is 49%, tartronate is 50%, glycolate is 22% and oxalate is 28%. In order to achieve higher selectivity to glycerate, milder oxidation of glycerol is required. We mentioned previously that increased pH in alkaline media promoted productions with high DOX through enhancing deprotonation/dehydrogenation of hydroxyls in glycerol and facilitating alkoxy intermediates formation. On the other hand, the acidic media probably favours products with low DOX. In combination with tuneable electrode potentials, glycerate may be generated with improved selectivity.

Figure 3a shows the product selectivity versus anode potentials on Pt/C catalyst after a reaction of 10 h at 60 °C in an acidic electrolyser.[103] When the applied anode potential is 1.097 V, the selectivity to glycerate reaches up to 87.0 % at 91.8 % glycerol conversion (Figure 3b).[103] More importantly, a glycerate selectivity of 80 % at 10 % glycerol conversion has been achieved in a practical continuous-flow electrocatalytic reactor (Figure 3c), which presents a great promise of Pt/C catalyst to efficiently convert glycerol into glycerate.[103] It should be noted that glyceraldehyde, which is easily oxidized to glycerate, can be obtained with a reasonable selectivity at low applied anode potential (i.e., ~48.8 % selectivity at 0.697 V in Figure 3a).[93,103]

By comparing the main products in alkaline and acidic media, it seems that the products on a Pt/C catalyst in acidic media and at high potentials present even lower DOX than that in alkaline media at low potential range. In this regard, high pH value in both alkaline and acidic media tends to generate high DOX products. This is likely due to i) the blocked active sites by specific adsorption of anions (i.e. SO_4^{2-}) in acidic media;[104] ii) the promoted oxidation of hydroxyl groups in glycerol to alkoxy by lowering the active barrier[98] in alkaline media; and iii) the enhanced oxidation kinetics when more OH_{ads} adsorbs on Pt surfaces because the oxidation of alcohol is governed by both $-RO_{ads}$ and OH_{ads}.[98]

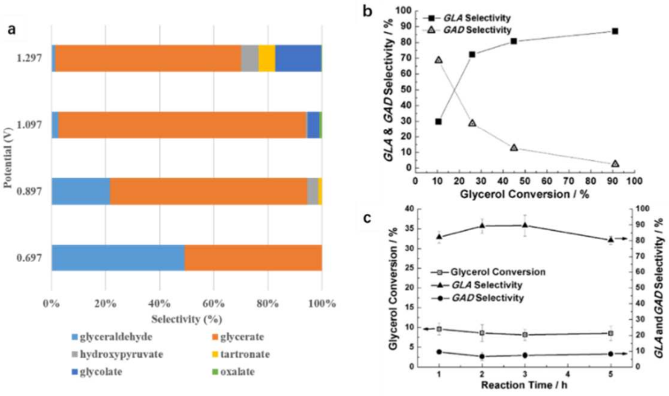

Figure 3. (a) Product selectivity after reaction for 10 h in 0.1 M glycerol and 0.5 M H_2SO_4 at 60 °C under different operating anode potential; (b) glycerol conversion vs. product selectivity over 20 wt.% Pt/C at the potential of 1.097 V; (c) Time-on-stream data of

continuous-flow reactor fed with 0.1 M glycerol at 0.18 mL min^{-1} (GLA and GAD represent glycerate and glyceraldehyde, respectively). Reproduced with permission from ref. 103. Copyright (2014) John Wiley & Sons, Inc

The above-mentioned products are all based on the preferential oxidation of terminal hydroxyls in glycerol. The oxidation of secondary/middle hydroxyls leads to the formation of dihydroxyacetone intermediate or product, which is widely employed as an important feedstock in pharmaceutical industry. However, the selective oxidation of secondary hydroxyls rather than the terminal ones is relatively more difficult, likely due to steric effect[105] and reaction probability (two in three are terminal hydroxyls in the glycerol). A successful example is to use a reversible Bi-modified Pt/C catalyst. The Pt/C catalyst produces dihydroxyacetone as the main product, even reaching a selectivity of 100% at ~0.4 V in Bi_2O_3-saturated (~10^{-5}-10^{-4} M) 0.5 M H_2SO_4 solution with 0.1 M glycerol.[67] At ~0.6 V, the concentration of products to dihydroxyacetone reaches maximum with a selectivity close to 90%.[67] This high selectivity is in clear contrast to the traditional thermal catalysis, in which the selectivity of only 63% is achieved for dihydroxyacetone production on Bi modified Au-Pt bimetallic catalysts.[65] This remarkable enhancement in selectivity highlights the advantages of electro-valorisation in some cases compared with the conventional thermal catalysis. Generally, it was found that the presence of Bi on Pt catalysts shows high selectivity to dihydroxyacetone at low potentials (0.4-0.8 V), to glyceraldehyde and glycerate at moderate potentials (0.8-1.3 V), and to formate and glycolate at high potentials (1.3-1.5 V).[67] However, on Pt/C without Bi, the selectivity to dihydroxyacetone is almost 0, where glyceraldehyde is main product at low potentials, and the selectivity for other products are similar with Bi modified Pt/C.[67] These facts indicate that Bi, which starts to desorb from Pt surfaces at 0.6-0.7 V,[106] is necessary for blocking terminal alcohol oxidation (probably changing the adsorption mode of glycerol[85]) and promoting dihydroxyacetone production (secondary alcohol oxidation). That is why the similar trend of products except dihydroxyacetone and glyceraldehyde are observed for Pt with and without Bi modification respectively at potentials >0.6 V. Although this report illustrates a possibility of tuning the oxidation of glycerol, the detailed reaction mechanism and structural information on electrocatalysts are still unclear and need further investigations. Some other reports employed PdBi for glycerol oxidation,[85,107-110] however, these papers did not report selectivity to products. In addition, the investigations using practical electrochemical reactors remains to be explored. Recently, a PtSb/C catalyst was reported as an efficient electrocatalyst for glycerol conversion to dihydroxyacetone,[111] indicating some secondary metals other than Bi are likely a promising promotor for selective oxidation of glycerol.

To summarize, Pt based catalysts present tremendous advantages in forming products with low DOX, such as dihydroxyacetone, glyceraldehyde, glycerate and tartronate etc., which can be facilely tuned by changing electrolyte pH values and applied potentials. Through appropriate surface modification, the selectivity to secondary hydroxyl oxidation is significantly improved.

3.2 Au based catalysts

The Au catalysts, which commonly present remarkably high resistance to CO poisoning[74-76,112,113] and kinetic promotion[112] during organic molecule oxidation, have also been studied for upgrading glycerol.[114] Interestingly, Au catalysts show almost no activity towards glycerol oxidation in neutral or acidic media.[115] Therefore, the following discussion is focused on alkaline media.

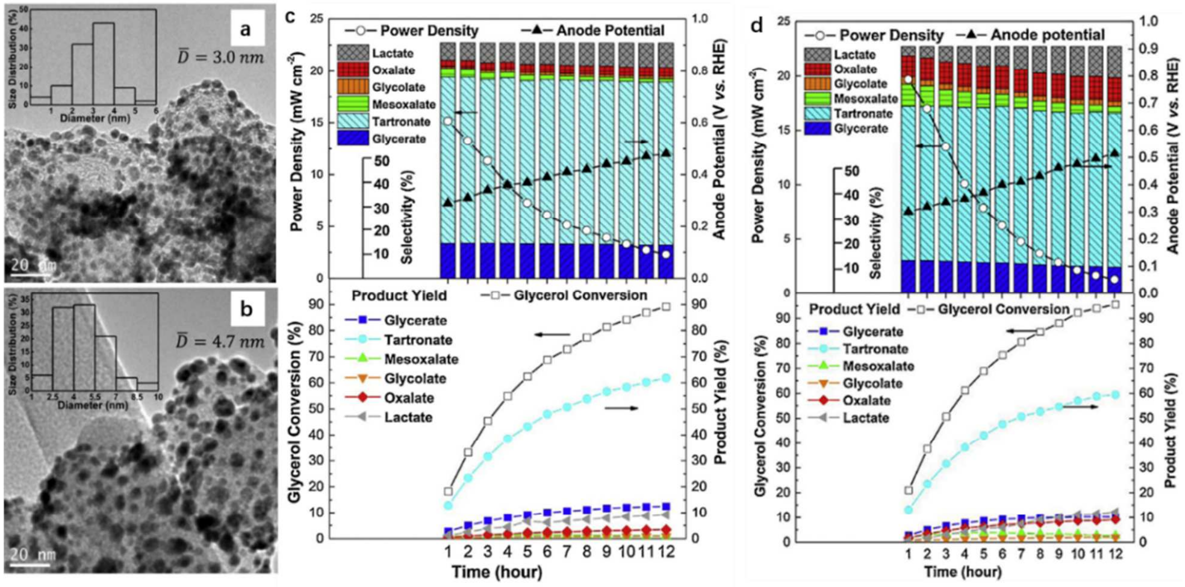

Figure 4. TEM images and particle size histograms of (a) Au/C-NC, (b) Au/C-AQ; and electrocatalytic selective oxidation of glycerol on (c) Au/C-NC (55 wt%) and (d) Au/C-AQ (55 wt%) in anion exchange membrane direct glycerol fuel cells under optimized condition for high yield of tartronate. Anode catalyst: Au/C-AQ or Au/C-NC (1 mg_{Au} cm^{-2}); cathode catalyst: Fe-Cu-

based catalyst (Acta 4020, 3 mg cm^{-2}), anion exchange membrane (A901, Tokuyama Inc.). Anode fuel: 8.0 M KOH + 1.0 M glycerol, 30 ml, 1.0 ml min^{-1}; cathode fuel: high purity O_2, 100 ml min^{-1}, ambient pressure. Glycerol:Au = 1:1300 (mol:mol); cell voltage: 0.1 V; cell temperature: 60 ◦C reaction time: 12 h. Reprinted with permission from ref. 35. Copyright (2014) Elsevier B.V.

Two types of Au catalysts prepared by organic phase nano capsule and aqueous phase method were denoted as Au/C-NC (Figure 4a) and Au/C-AQ (Figure 4b), respectively, which were then applied in cogeneration fuel cells.[35] The Au/C-AQ catalyst shows an averaged particle size of 4.7 nm, larger than that of Au/C-NC (3.0 nm)[35] due to the efficient protection by organic stabilizer (oleylamine) from agglomeration.[116] Both Au catalysts mainly produced tartronate (approximate 70% selectivity on Au/C-NC in Figure 4c and 60% selectivity on Au/C-AQ in Figure 4d) at 0.3~0.5 V.[35] This result is different from that on Pt, on which a mixed glycerate and tartronate were produced at the similar potential range (Ref. 34, section 3.1).[34] The high selectivity to tartronate rather than a mixed glycerate and tartronate indicates the more facile oxidation of glycerate to tartronate on Au catalysts than that of Pt. In addition, after 12 h operation under same conditions, the Au/C-AQ catalyst presents a glycerol conversion of 95.6% (Figure 4d), which is much higher than that on Au/C-NC (89.2% Figure 4c).[35] The low efficiency of Au/C-NC could be attributed to the residual hydrophobic ligands from oleylamine that may block the active sites,[116] which probably decreases the retention time of reactants/intermediates, leading to less active sites for further electro-oxidation and higher selectivity to tartronate rather than other high DOX products.[35] Although this paper did not analyse the effects of Au particle size on product selectivity, it is hypothesized that the catalyst size is probably another factor that needs to be further investigated.

At higher electrode potentials, products with higher DOX were generated on Au catalysts,[117] similar trend to that on Pt. As the anode potential increases from 0.35 to 0.65 V, selectivity to mesoxalate increases from ~0% to 57% at the expense of tartronate (drops from 79% to 26%) on Au/C in 2.0 M KOH + 1.0 M glycerol at 50 °C for 1 h.[117] Further increasing the applied anode potential on Au catalyst, however, will lead to the C-C bond cleavage. For example, over 40 wt% Au nanoparticles (2.5 nm) supported on carbon nanotubes (CNT) (Figure 5a and 5b), a high selectivity to glycolate (85%) was observed at the potential of 1.6 V (Figure 5c).[87] Other previous independent reports also support this conclusion.[78,79,118] In addition to the applied potentials, the influence of pH value and reactant concentration on the selectivity on Au catalysts shows a similar trend as those on Pt catalysts.[87] Recently, the support and loading of Au were also reported to influence the product selectivity albeit to a lesser extent.[119]

Compared with Pt-based catalysts, the Au-based catalysts show more products with higher DOX including tartronate, mesoxalate and even C-C cleavage products such as glycolate and oxalate etc, indicating Au promotes oxidation reactions of hydroxyls and C-C cleavage of glycerol.

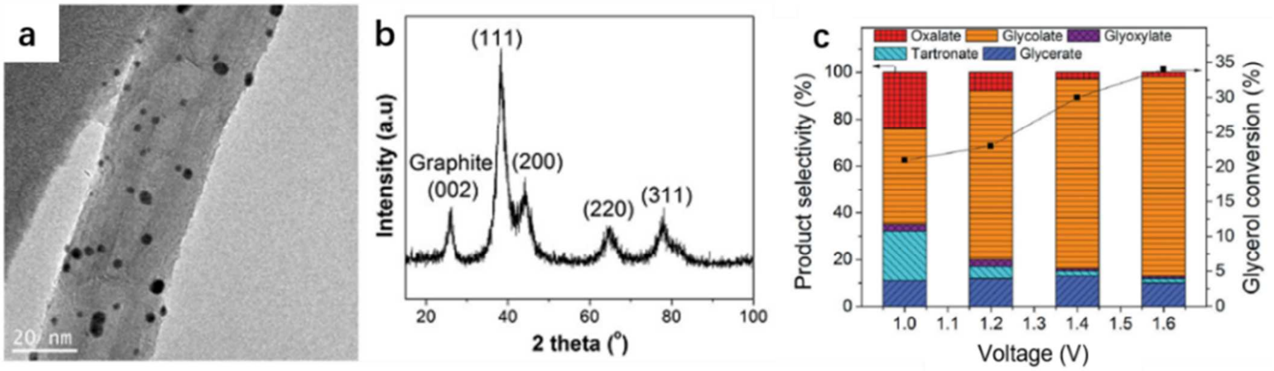

Figure 5. (a) TEM image and (b) XRD pattern of Au/CNT; (c) electro-oxidation of glycerol (2.0 M KOH + 1.0 M glycerol) on Au/CNT catalyst under different applied potentials for 3 h at room temperature. The pictures are taken with permission from ref. 87. Copyright (2012) The Royal Society of Chemistry.

3.3. Pd based catalysts

Compared to Pt and Au based catalysts, Pd based catalysts generally present lower barrier for C-C bond cleavage and higher oxidative activity toward high DOX products such as formate. Indeed, ~ 7 % formate was found on Pd/C catalyst at 0.8 V in 0.1M NaOH (supporting information of ref. 120), whereas almost none was observed in higher basic concentrations (0.5-4.0 M KOH) on Au/C catalyst even at a potential up to 1.0 V.[87] Over Pd/C catalyst at 0.8 V, glycerate and glycolate were the dominant products in 0.1 M NaOH,[120] indicating that the Pd based catalysts probably efficiently promote the oxidation of terminal hydroxyls and C-C bond cleavage.[120-123] Notably, the introduction of Sn[124,125] and/or employing nitrogen doped carbon as the supports[126] in Pd based composite catalysts could inhibit the C-C bond cleavage and thus lead to favourable production of C3 compounds.

3.4 Summary of glycerol oxidation on Pt, Au and Pd based catalysts

Table 1 summarizes the product selectivity in electrochemical devices/reactors on the precious metal catalysts as discussed above. In general, the potential is an important factor affecting the reaction pathway, i.e. higher applied anode potential results in products with higher DOX on the same catalysts. Despite of the highly debated reaction mechanisms, some general trends for glycerol electro-oxidation in alkaline/acidic media can be summarized on the Pt, Au and Pd based catalysts, as shown in Figure 6.[119,127,128]

Table 1. The main products on several typical catalysts.

Catalysts	Potential	Media	Temperature	Main Products	References
Pt	<0.5 V	KOH	50 °C	Glycerate & Tartronate	34
Pt	0.697 V	H_2SO_4	60 °C	Glyceraldehyde & Glycerate	103
Pt	1.097 V	H_2SO_4	60 °C	Glycerate	103
Pt-Bi	0.4~0.6 V	H_2SO_4	Room temp.	Dihydroxyacetone	67
Au	0.3~0.5 V	KOH	60 °C	Tartronate	35
Au	0.65 V	KOH	50 °C	Mesoxalate	117
Au	1.0 V	KOH	Room temp.	Glycolate & Oxalate	87
Au	1.6 V	KOH	Room temp.	Glycolate	87
Pd	0.8 V	NaOH	Room temp.	Glycolate & Glycerate	120

Generally, glycerol electro-oxidation goes through Route I (blue pathways in Figure 6) on Pt, Au and Pd catalysts, during which the terminal hydroxyl is initially oxidized. Over Bi modified Pt catalyst, however, oxidation of internal secondary hydroxyl groups (route II, yellow pathways in Figure 6) is favoured to produce dihydroxyacetone in acidic media. Through Route I, Pt and Au based catalysts tend to produce C3 products due to the low activity and selectivity for C-C bond cleavage. Compared with Pt, however, Au catalysts favour the production of C3 compounds with higher DOX. At higher applied potentials (i.e., mainly glycolate product at 1.6 V[87]), C-C bond cleavage will be promoted on Au catalyst toward the production of C2 chemicals. In addition, glycerol is probably oxidized directly rather than going through the glyceraldehyde intermediate to glycerate on Au catalysts, followed by the successive oxidation of glycerate to tartronate/mesoxalate or glycolate depending on the applied potentials. The reaction pathway to the oxalate formation is still unclear on Au catalysts. On Pd catalysts, direct or indirect glycerol oxidation are proposed to produce glycerate, which is then converted into glycolate via C-C bond cleavage.

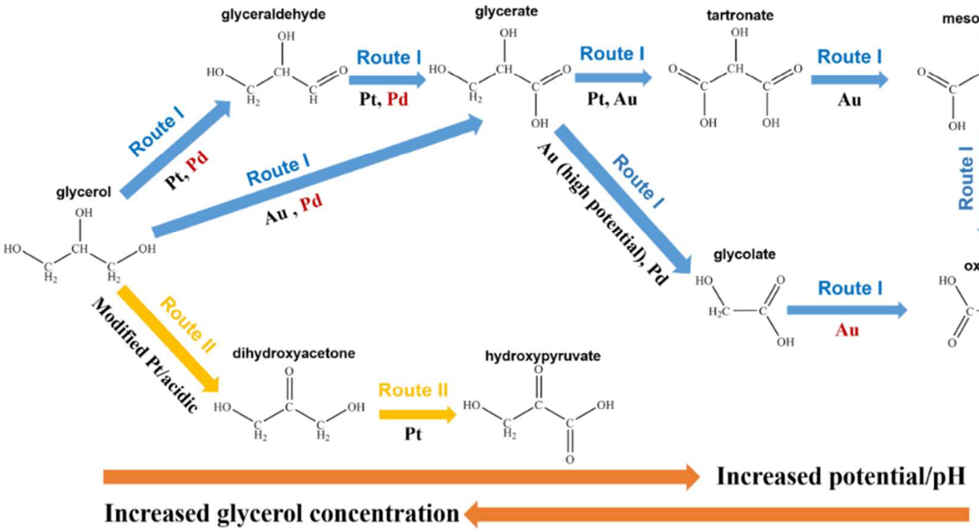

Figure 6. Glycerol and its partial products after electro-oxidation (black: carbon; red: oxygen; white: hydrogen) on various precious catalysts mainly in alkaline media (red words mean uncertain routes on certain catalysts).

Based on the above discussions, the nature of catalysts (Pt, Au and Pd) is the dominant factor for selectivity, which probably affects the form of adsorbed glycerol and binding energetics. However, the effects of nanoscale factors such as facets, size distributions and catalyst-support interactions etc. on glycerol electro-valorisation remain to be explored. Learning from catalyst design/synthesis for other electrocatalysis systems including ORR, OER and HER etc., the properties such as compositions (e.g. incorporation of secondary transition metal etc.),[129-133] nanostructures (e.g. core-shell and hierarchical porous structures),[134-136] preferential facets[137-140] and supports (e.g. strong catalyst-support interactions etc.).[141,142] are likely helpful to tune electrochemical activity, durability and mass transfer.[143] Thus rational design of electrocatalysts is expected to further optimize the conversion and selectivity for biomass upgrading.[144] In addition, higher pH values/potentials and lower glycerol concentrations facilitate deep oxidation of glycerol, which lead to the formation of high DOX products such as glycolate, mesoxalate and oxalate depending on the catalysts employed (Figure 6). It is expected that by tuning pH, the adsorbed OH_{ads} could be optimized, accelerating hydroxyl oxidation to alkoxy groups by both thermodynamics (lowing active barrier) and dynamics (increasing oxidation kinetics). Together with the applied electrode potentials, biomass-derived intermediates with hydroxyls can be valorised to value-added products in a controlled way.

3.5 Non-precious catalysts

Although the precious metal catalysts show promising performances in glycerol valorisation, the high cost limits their practical applications. In addition to precious metal catalysts, several investigations employed low cost transition metal catalysts, such as Ni-based catalysts.[145-149] Recently, the products including glycerate, glycolate, tartronate and oxalate have been reported on Ni-based alloy (NiFe, NiCo, NiFeCo) catalysts although the reported selectivity is still lower compared with Pt, Au and Pd based catalysts.[150] However, it is notable that the Ni-based catalysts are not stable in alkaline media at high potentials, e.g. 1.6 V in ref. 150. Therefore, the real catalysts for glycerol oxidation in the cases should be Ni-based (oxy)hydroxides. In this regard, some transition metal based (oxy)hydroxides are likely promising in handling glycerol upgrading. Moreover, TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl), a known mediator in homogeneous catalysis, was found to be a good promotor to produce dihydroxyacetone on glassy carbon electrodes in $NaHCO_3$ media. In particular, longer reaction time results in comparable amounts of hydroxypyruvate, which could be generated by precise oxidation of dihydroxyacetone (Route II in Figure 6).[151] This work bridges the homogenous and heterogenous catalysis, which is a unique and efficient strategy in electro-valorisation of biomass-derived chemicals. To the best of our knowledge, there has been no report yet on non-precious metal catalysts in electro-valorisation of glycerol in practical electrochemical reactors. So far, there have been very limited investigations on non-precious catalysts for glycerol oxidation, which deserves more effort in the future.

4. Electro-valorisation of 5-hydroxymethyl-2-furfural (HMF)

Cyclic compounds are another key biomass-derived product. Unique structures of furan rings and branches make it possible to be either oxidized or reduced, most products of which are important raw materials for fine chemical industry. 5-hydroxymethyl-2-furfural (HMF) is one of the main five-membered heterocyclic molecules derived from biomass,[5,152,153] which contains furan rings, −C=O and −OH groups, and has been intensively investigated using electrocatalytic approaches.[17] A recent review systematically summarized progresses related to furanic compounds conversion with a focus on metal catalysts and homogeneous catalysts.[17] In this section, we mainly discuss typical precious metal catalysts and new advances using phosphide as electrocatalysts in understanding the effects of catalyst natures on the electro-valorisations of HMF. We also discuss possible competitions between HER and HMF electro-reduction.

4.1 Electro-oxidation of HMF on precious catalysts

An HMF molecule consists of furan rings, aldehyde and hydroxyl functional groups that can be oxidized through aldehyde oxidation and/or hydroxyl oxidation processes into several value-added chemicals such as 5-hydroxymethyl-2-furan carboxylic acid (HFCA), 2-formyl-5-furan carboxylic acid (FFCA), 2,5-Furan dicarboxylic acid (FDCA), and 2,5-furan dicarbaldehyde (FDC) etc. (Figure 7).[17,154]

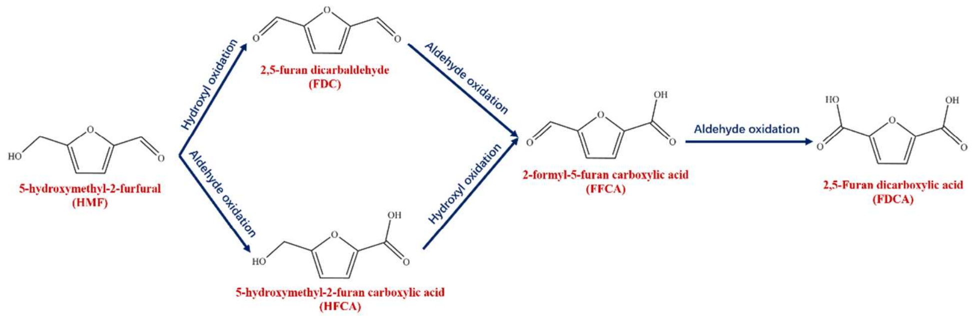

Figure 7. Schematic illustration of HMF and its products.

Similar with the glycerol electro-oxidation, the electro-oxidation from HMF to FDCA typically requires metallic catalysts such as Au, Pd, and Pd-Au alloy.[17] On Au/C catalysts, the major product is HFCA (98% selectivity) at potential from 0.6 to 0.9 V, indicating that initial aldehyde oxidation (Figure 7) was favoured on Au, and higher potential (1.2 V) was required for further hydroxyl branch oxidation to FFCA and aldehyde oxidation to FDCA (selectivity to FFCA and FDCA are 5% and 14%).[154] Differently, Pd/C catalysts achieved higher FDCA selectivity at both 0.6 V and 0.9 V, where the major products are FFCA (64%) and HFCA (70%), respectively.[154] This observation indicates that HMF oxidation on Pd/C probably follows two competitive pathways including FDC (lower potentials) and HFCA (higher potentials) as intermediates, which depend on the potential ranges. Note that alloying Au and Pd is found to change HMF oxidation mechanisms. Figure 8a presents Pd-Au alloy nanoparticles supported on carbon black. This catalyst was employed as anode catalysts in an alkaline flow reactor at 25 °C. The product distribution at different applied potential after 1 h reaction was analysed and plotted in Figure 8b. Interestingly, the selectivity to FDCA shows a "volcanic curve" *vs.* applied potentials. When the applied potential is increased from 0.5 to 0.9 V, the selectivity to FDCA increases,[154] which can be attributed to enhanced HFCA selectivity, quickly producing FFCA and successive FDCA at high potentials, and probably optimized reacting pathways by Au and Pd. At 0.9 V, the molar selectivity of FDCA reaches up to a maximum of 83%, after which the FDCA selectivity decreases with further increased potentials, probably due to the surface oxidation of metal atoms, and thus deactivation of the active sites for FDCA production. Since the oxidation sequence of these products is HFCA→FFCA→FDCA or FDC→FFCA→FDCA (Figure 7), it is still unclear why Pd-Au alloy significantly enhances the selectivity to FDCA and whether the reaction goes through FDC intermediate or not since almost no FDC was detected.[154]

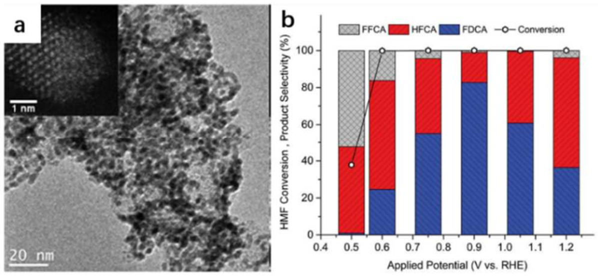

Figure 8. (a) TEM image of Pd_1Au_2/C (b) Product distribution on Pd_1Au_2/C for the oxidation of 0.02 M HMF in 0.1 M KOH. Reaction conditions: 1 h; AEM-electrolysis flow cell; 25 °C.[154] Copyright (2014) The Royal Society of Chemistry.

From the discussions above, the combination of Pd and Au significantly improves the oxidizing ability towards HMF to FDCA in terms of tuned electronic structure, modified reaction pathways or other unknown mechanisms. It enlightened that the selectivity to FDCA can be improved by introducing a secondary component in nanostructures.

4.2 Electro-oxidation of HMF on non-precious catalysts

In ref. 39, TEMPO was used as a mediator in an electrochemical cell, achieving almost 100% yield to FDCA from HMF at 1.54 V. TEMPO is a representative non-precious homogeneous catalyst. In comparison with homogeneous catalysis, heterogeneous catalysis has the advantages of facile product separation, high stability. Recently, non-precious catalysts such as phosphide[38,155] and sulphide[156] have been investigated for converting HMF into FDCA (Figure 9a). For instance, ~100% HMF conversion and ~90% yield to FDCA were achieved on CoP at 1.423 V in 1.0 M KOH media under atmosphere conditions (Figure 9b), while hydrogen was produced at cathodes simultaneously.[38] Notably, at such a potential, oxygen evolution reaction does not taken place. In addition, this work integrated both HMF oxidation at anodes and H_2 evolution at cathodes in an electrolyser with the same CoP catalysts at both sides. The required voltage to achieve a current density of 20 mA cm^{-2} was only 1.44 V, which is 150 mV lower than water splitting.[38] This report successfully integrates the electro-valorisation of biomass and HER by replacing sluggish OER with value-added HMF oxidation reaction, which could be an important approach for the future applications. In addition, the HMF oxidation mechanisms on CoP catalysts seem to be different from that with TEMPO (Figure 9c).[39] During TEMPO-mediated electrocatalytic HMF oxidation, FFCA apparently accumulated and reached maximum until the FDCA started to form (Figure 9c).[39] FDCA was formed immediately after starting electrolysis in CoP-catalytic processes (Figure 9b).[38] However, the fundamental reasons for the significantly enhanced selectivity are still unclear; further effort is needed to understand the mechanisms of HMF conversion.

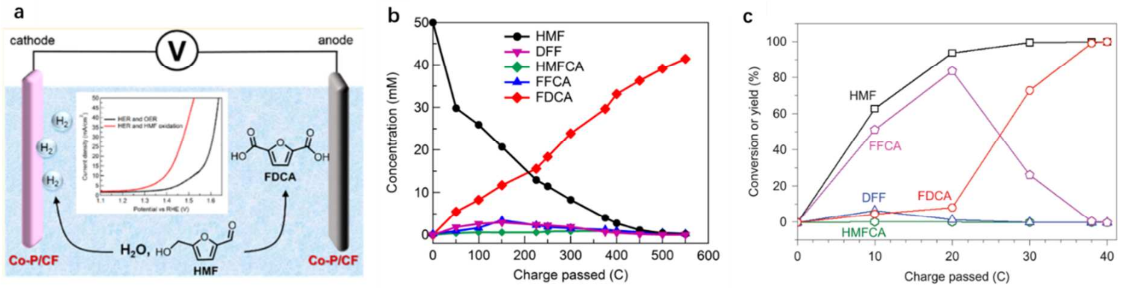

Figure 9. (a) Schematic of the electrochemical cells with Co-P/CF catalyzed HMF oxidation; (b) concentrations of HMF and oxidation products over passed charge during the chronoamperometry experiment conducted at 1.423 V in 1.0 M KOH containing 50 mM HMF;[38] Copyright (2016) American Chemical Society. (c) Conversion and yield (%) changes of HMF and its oxidation products during the electrochemical oxidation of HMF at 1.54 V in a 0.5 M borate buffer solution containing 5 mM HMF and 7.5 mM TEMPO (DFF and HMFCA represent same products FDC and HFCA in this paper, respectively).[39] Copyright (2015) Macmillan Publishers Limited, part of Springer Nature.

It is noteworthy that HMF can be converted to FDCA with a selectivity of around 80 % on Au/TiO_2 catalysts by traditional thermal catalysis,[157] which is much lower than the above-mentioned electrocatalytic conversions. In addition, in the above electrocatalytic conversions, non-precious metal electrocatalysts were used which could significantly decrease the cost. To summarize it, the electro-valorisation provides a better solution for HMF conversion with lower cost than traditional technologies such as thermal catalysis.

4.3 Electro-reduction of HMF: in competition with HER

The electro-reduction of HMF usually includes hydrogenation and hydrodeoxygenation reactions.[17] The hydrogen can be directly extracted from the electrolytes (i.e., water, H^+ and OH^-), eliminating the requirement of external hydrogen supply as opposed to the thermal catalysis. However, it is a great challenge to control the competitive reactions between HER and the hydrogenation of furan rings/aldehyde branches or hydrodeoxygenation of aldehyde/hydroxyl branches on the catalyst surfaces. Therefore, efforts should be made to lower HER activity/selectivity (i.e., increase HER overpotential). This should be emphasized, but effective approaches are rarely reported.[17] Herein, some insights regarding the competition between HER and electro-reduction of HMF, are provided.

It is well known that the Pt group metals (PGM) show much lower overpotential for HER, i.e. probably high selectivity to HER. HER is thus expected to take place simultaneously if these metals or catalysts with low hydrogen-evolution overpotential are employed. From this point, catalysts such as Fe, Ni, Cu, Ag, Pb etc. metals (mostly non-PGM metals) with medium/high HER overpotential are good choices for electro-reduction of biomass-derived intermediates.

A series of non-PGM metals were investigated for the conversion of HMF to 2,5-dihydroxymethylfuran (DHMF) by aldehyde hydrogenation. It was found that the production of DHMF strongly depends on the catalysts and pH of solution: metals such as Fe, Ni, Cu, and Pb are beneficial for DHMF generation in acidic solution,[158] while the Fe, Ni, Ag, Zn, Cd and In work well for DHMF production in neutral media.[159] An interesting fact is that the presence of glucose not only enhances the formation of DHMF but also suppresses the hydrogenolysis of HMF in such 0.1 M Na_2SO_4 solutions,[159] the reason for which is unclear yet.

Ag electrode with dendritic fractal morphology has been successfully prepared on Cu substrate *via* galvanic displacement (Figure 10a). The high-surface-area Ag electrodes catalyst selectively produced DHMF in borate buffer (pH 9.2) solution.[160] After cathodic polarization at −0.56 V for a while, the Faradaic efficiency and selectivity for DHMF formation were both ~99%,[160] indicating that HER and other competing reactions are negligible. Notably, the Ag electrodes are stable after polarization (Figure 10b). Moreover, the applied potential range significantly affects Faradaic efficiency and yield. At a lower potential range between -0.36 and -0.26 V, both Faradaic efficiency and selectivity for DHMF are low, due to the side-reaction consuming HMF.[160] However, when the potential is decreased to lower than -0.36 V, where hydrogen atom adsorption starts to take place in the absence of HMF, the Faradaic efficiency and selectivity to DHMF increase and reach up to ~100% at -0.56 V, confirming the possible synergy between adsorbed hydrogen and HMF conversion.[160] Upon further decreasing the potential, hydrogen coverage increases, which can suppress the adsorption of HMF molecule. When the applied cathodic potential is lower than -0.86 V, while the selectivity to DHMF remains high (more than 97%), the Faradaic efficiency for DHMF decreases rapidly (low than 90%), due to the competing HER.[160] Although more electric energy will be consumed in the high overpotential ranges, the conversion rate of DHMF is much higher than that in low overpotential ranges.[160]

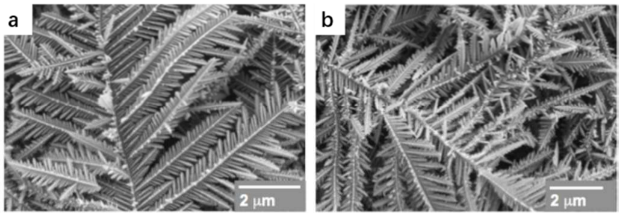

Figure 10. SEM images of Ag electrodes (a) as-deposited and (b) after polarization at −0.56 V for HMF reduction.[160] Copyright (2016) American Chemical Society.

Electrochemical operation protocol is another potential way to suppress HER. Recently, a half-wave rectified alternating current (a.c.) electrochemical method (a.c. voltage of −5 V to 0 V with a frequency of 400 Hz) using an amidoxime-functionalized carbon electrode was proposed to extract uranium element from sea water, which avoids side reactions involving ions such as Na^+, Ca^{2+} etc. in sea water.[161] The suppression of side reactions can be attributed to modifying amidoxime that can provide chelation sites for preferable binding to targeted uranyl ions and reduced/deposited charge-neutral species, e.g. (UO_2); On the other hand, the voltage that alternates between cathodic polarization and zero leads to extraction of uranium and releasing of other ions without specific binding, respectively.[161] During these processes, water splitting was remarkably suppressed by enhancing the frequency at high voltage (-5 V) (see Supplementary Figure 2 in ref. 161). This work provides a promising strategy to improve selectivity by modifying electrodes to enhance the binding ability to targeted value-added productions and suppressing unfavourable side reactions including HER by employing alternating current. Moreover, further investigations particularly theoretical modelling is still needed to understand the electrocatalytic hydrogenation/hydrodeoxygenation. The adsorption free energy is considered a good descriptor for catalyst activity. For example, adsorbed H (H*) is regarded as a main intermediate during HER. The adsorption free energy of H*, i.e. ΔG_{H*}, is thus a descriptor to estimate the adsorption strength on different catalysts.[129,162] $\Delta G_{H*}<0$ indicates strong binding of the intermediate, leading to occupied active sites and poisoning; meanwhile, $\Delta G_{H*}>0$ means weak binding, leading to barrier of intermediate activation.[143,163] Both of them decrease HER exchange current densities and $|\Delta G_{H*}|\approx 0$ is thus a necessary but insufficient factor for high HER activity.[143,164] $|\Delta G_{H*}|>>0$ on different catalysts is a good parameter to screen catalysts with high barrier for HER, i.e. probably good for targeted electro-reduction reactions. Similarly, some suitable descriptors like $\Delta G_{\text{intermediates}}$ for intermediates of biomass conversion also need to be established. The integration of ΔG_{H*} and $\Delta G_{\text{intermediates}}$ should be proposed to screen good catalysts for electro-reduction of biomass-derived chemicals.

5. Concluding remarks

Electrocatalytic conversion is promising to produce value-added chemicals from biomass-derived platform chemicals due to the mild operation condition, high conversion efficiency/selectivity and scalability. It also allows to store renewable energy at large scale. We reviewed the electro-valorisation of glycerol and 5-hydroxymethyl-2-furfural, as affected by catalysts, electrochemical systems, electrocatalytic operation parameters such as electrode potentials and electrolytes (particularly pH values).

In addition to the advantages of electrochemical oxidation of biomass intermediates as discussed above, electrocatalysis also shows promises for electrochemical hydrogenation (i.e., reduction process). For example, electrocatalysis presented a much higher TOF of 3899 h^{-1} towards hydrogeneration of benzaldehyde to benzyl alcohol on Pd/C compared with thermal catalysis (1062 h^{-1}).[165] The activation energies of benzaldehyde hydrogenation through electrocatalysis were lower than thermal catalysis.[165] However, there are still some scientific challenges and technology gaps for practical applications in terms of selectivity, efficiency and conversion rates.

There has been very limited fundamental understanding on catalyst composition/structure-property relationship regarding electro-valorisation of biomass (e.g. how does a secondary metal, metal size distribution, preferential facet, porous structure, metal composition/segregation etc. affect biomass valorisation and the underlying mechanisms), which is the foundation for rational design of catalysts.[144,166,167] Moreover, organic biomass molecules such as glycerol and HMF etc. are more complicated, conversion of which involve much more electrons than other electrocatalytic reaction such as HER, ORR/OER. In this regard, electro-valorisation of biomass intermediates can be more challenging compared with the relatively simple HER, ORR/OER because of the abundance in intermediates, for which a good model system will be even more crucial. Combination of advanced characterization tools (e.g. *in situ* characterizations for both products and electrode/electrolyte interfaces)[168-170] and theory will also be very helpful to revealing underlying reaction mechanism and interface evolution. Homogenous electrocatalysis using mediators also shows great potential for electro-valorisation.[171] For example, allylic C–H bonds oxidation has been successfully achieved by homogenous electro-catalysis, presenting not only scaled-up production (demonstrated on 100 grams) but also broad choice of substrates.[16] However, a greater challenge for homogenous catalysis is the separation of catalysts and products.

We should point out that biomass upgrading involves many types of molecules, including furfural,[172-175] phenol,[176-178] cellulose,[179] lignin,[180-182] levulinic acid,[183-186] ethers,[187] aldehydes,[188] alcohols,[189] ketones,[190] quercetin,[191] sugar alcohols,[192-196] sugars,[118,197-201] etc. Therefore, electrocatalytic conversion of biomass derived chemicals is a broad open space for exploration. Furthermore, photocatalysis[39] and biocatalysis[202] can be integrated with electrocatalysis, i.e. photoelectrocatalysis and bioelectrocatalysis, for biomass valorisation. Photocatalysis is a promising strategy to directly utilize clean solar energy to upgrade biomass-derived chemicals,[39] which likely accelerates the kinetics/selectivity by employing photogenerated electron-hole pairs; while biocatalysis shows possibility for researchers to learn from biology such as bacteria that is an existing model for certain conversion processes (e.g. CO_2 reduction[202]). A multidiscipline approach involving electrochemistry, photochemistry, biology, material and catalysis etc. can be developed for more efficient electro-valorisation of biomass-derived intermediates. By taking advantage of knowledge and advanced experimental and theoretical tools that have been developed for other electrocatalysis systems such as ORR, OER, HER for the past decades,[129,134,135,137-139,141-143] biomass electrocatalysis could potentially provide great opportunities for scientific discovery and technological development. It could play an important role for developing a sustainable society, particularly for electric grid and chemical/fuel industries by storing renewable electric energy and producing key feedstock chemicals.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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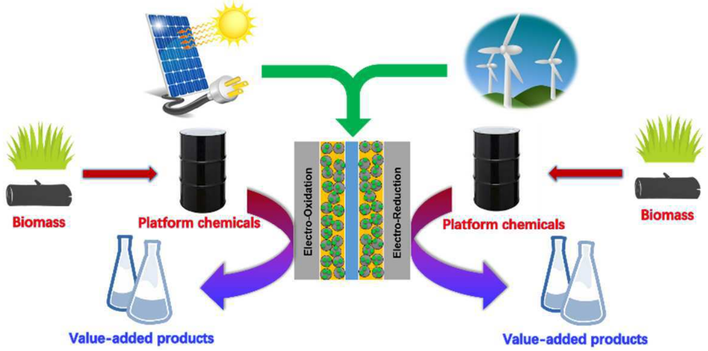

Recent progresses in electro-valorization of biomass-derived intermediates are reviewed, while a perspective on future R&D in this field is provided