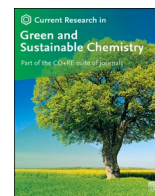




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## Additive manufacturing technologies applied to the electrochemical valorization of biomass

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### ABSTRACT

Biomass valorization is gaining recognition as a sustainable and easily accessible renewable option to produce fuels and chemicals non-derived from fossil fuels, thus contributing to the decarbonization of the energy and chemical industries. Electrosynthesis represents a potent and advantageous method to transform biomass-based compounds into added-value products, surpassing conventional synthetic pathways in various aspects. Nevertheless, technical and geometrical constraints preclude its widespread implementation and development. Within this context, additive manufacturing has the potential to emerge as a disruptive technology in the field of electrochemical reactions, enabling the creation of custom-designed cells and reactors with intricate geometry. This perspective article delves into the applications of this innovative and widely accessible technology in organic electrosynthesis for biomass valorization, highlighting its potential to enhance performance, optimize mass transport phenomena, and facilitate the design of efficient and scalable electrochemical systems for various applications.

### 1. Introduction

As industries strive to reduce greenhouse gas emissions and mitigate climate change, there is a growing need for sustainable and renewable energy sources. This transition entails a shift from fossil fuel-based energy systems to cleaner alternatives such as renewable electricity, hydrogen, and bioenergy [1,2]. In this context, biomass emerges as a promising and accessible renewable alternative to fossil fuel-based energy sources. Biomass is considered a carbon-neutral energy source because the carbon dioxide released during its combustion is offset by the carbon dioxide absorbed by the plants during growth [3].

With the aim of harnessing the potential of biomass as a renewable and sustainable platform to produce high-value chemicals, research efforts are focusing on exploring the potential of furfural and 5-hydroxymethylfurfural (HMF) as versatile intermediates in the context of biomass utilization. Furfural and HMF (Fig. 1a) are compounds derived from carbohydrates found in biomass feedstocks and they have garnered attention as building blocks for the synthesis of valuable chemicals and materials [4,5]. Various conversion pathways enable the transformation of furfural and HMF into biomass-derived polymeric materials, precursor compounds for furanic biopolymers, and renewable furan resins [6,

7].

Another interesting biomass resource is lignin (Fig. 1b), which is a complex organic polymer found abundantly in the cell walls of plants. Often considered a byproduct in the pulping and paper-making industries, lignin has gained attention for its role in biomass valorization [8]. Lignin can be harnessed as a feedstock for the production of bio-based chemicals, materials, and biofuels through various biorefinery processes, contributing to a more sustainable and circular economy [9].

Glycerol (Fig. 1c) is emerging as an important resource in promoting sustainability and circular practices within the industry. Following the transesterification process commonly used in biodiesel production, significant quantities of glycerol are generated as a byproduct. This glycerol waste can be effectively harnessed as a valuable feedstock for the production of a wide range of high-value chemicals. For instance, within a direct glycerol fuel cell, this resource enables the simultaneous generation of added-value products and electrical energy. Alternatively, in an electrolyzer setup, the synthesis of chemicals from glycerol can be powered by renewable energy sources, further contributing to a greener and more sustainable future [10].

In recent years, electrosynthesis has been recognized by the chemical community as a powerful synthetic approach due to its numerous

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advantages over traditional synthetic routes such as providing a sustainable synthetic approach while limiting at the same time side reactions and catalyst deactivation promoted by chemical redox reagents [11]. In a minimalistic electrochemical cell configuration, typically a two-electrode setup, an anode and a cathode, are immersed into a solution containing the organic substrate(s) and a supporting electrolyte, which is required to increase the conductivity of the solution. Applying a potential difference between the electrodes allows oxidation and reduction reactions to occur, using an external power source [12]. This approach offers improved reaction selectivity, enabling the formation of desired products while minimizing unwanted by-products. It also allows for milder reaction conditions, reducing the need for harsh chemicals or high temperatures [13]. Moreover, electrosynthesis can offer greater control over reaction parameters and it provides opportunities for sustainable and environmentally friendly synthesis by utilizing renewable energy sources and minimizing waste generation [14].

Continuous-flow reactor technology is gaining interest in academia and industry because enables the development of highly efficient synthetic protocols that improve performance by reducing heat and mass transfer limitations, improving contact between reagents, catalysts and other important reactor surfaces (e.g., electrodes) [15]. Typically, these systems work by continuously feeding reagents to a reactor system through a number of inlets and removing the products through outlet streams. The distribution of flow in a single or multi-phase fashion is critical for the efficiency of the reactors and the transformations undertaken. The design of reactors is typically constrained by manufacturing technologies. In electrochemical reactors, parallel plate electrodes with or without membranes are normally preferred due to the simplicity of assembly. Innovative designs in electrochemical reactors have demonstrated to improve the reactor performance [16–18].

Additive manufacturing (AM), commonly known as 3D printing, is an enabling technology that builds objects layer by layer, allowing for elaborate designs and complex geometries. It works by using computer-aided design software to slice a digital model into thin cross-sectional layers, which are then sequentially printed using various materials and deposition methods, such as fused deposition modelling, selective laser sintering or vat photopolymerizable resins [19]. This technology, also known as 3D printing (3DP), has offered numerous advantages across various research fields. For example, in medicine and healthcare, it has enabled the creation of patient-specific implants and drug delivery systems [20]. In engineering, it has facilitated rapid prototyping allowing for iterative design improvements and reducing development time [21]. In materials science, it has enabled the fabrication of complex structures with tailored properties [22]. 3D printing has allowed to

accelerate innovation, foster customization, and open up new possibilities in a wide range of disciplines. In reactor engineering, the use of 3DP to produce continuous-flow reactors was demonstrated for the first time little over a decade ago [23,24]. Since then, the field has experienced a significant growth with multitude of developments employing multiple techniques, reactor architectures and applications [25].

The integration of 3DP with organic electrosynthesis has introduced several advantages to the field by leveraging 3DP design flexibility and precision. Researchers have created custom electrochemical reactors with intricate geometries that enable enhanced control over reaction parameters, leading to improved selectivity, yield, and overall performance [26,27]. Traditional H-cell reactors have been widely used in electrochemistry, even though these cell configurations often present mass-transport limitations. This parameter is critical for the kinetics of organic electrosynthesis, and it is typically enhanced by using flow cells that allow for the integration of turbulence promoters, and improved mass transfer by design [13,28–31].

This contribution primarily focuses on the latest trends found in the literature, highlighting potential areas of growth for electrochemical biomass valorization utilizing continuous-flow and 3D printed reactors. The review is divided into the following sections: (i) biomass valorization reactions; (ii) continuous flow applied in biomass valorization reactions (iii) 3D printed reactors applied to electrosynthesis; (iv) conclusions and perspectives.

## 2. Biomass valorization reactions

Biomass conversion is a very important topic these days. Many important products are obtained from biomass, among which furanic derivatives are the most promising ones as they can be used as building blocks in the chemical industry [32]. In particular, oxidation of furfural and HMF produces carboxylic acid type species such as furanic acid and 2,5-furan dicarboxylic acid (FDCA), that are used in the polymer industry [33]. Interesting compounds can also be obtained from the reduction of furfural and HMF, like furfuryl alcohol and bis-hydroxymethylfurfural (BHMF), which are reaction intermediates in the pharmaceutical and polymer industries, and 2-methyl furan (MF) and 2,5-dimethylfuran (DMF) that are promising as biofuels.

Electrochemistry is a useful methodology for the conversion of biomass due to the advantages of working under mild reaction conditions (i.e., ambient temperature and pressure). By controlling the potential-current parameters, solvents, electrolytes and types of electrodes it is possible to improve the reaction rate and the selectivity of the reactions. In the hydrogenation reaction, it is possible to use water as the

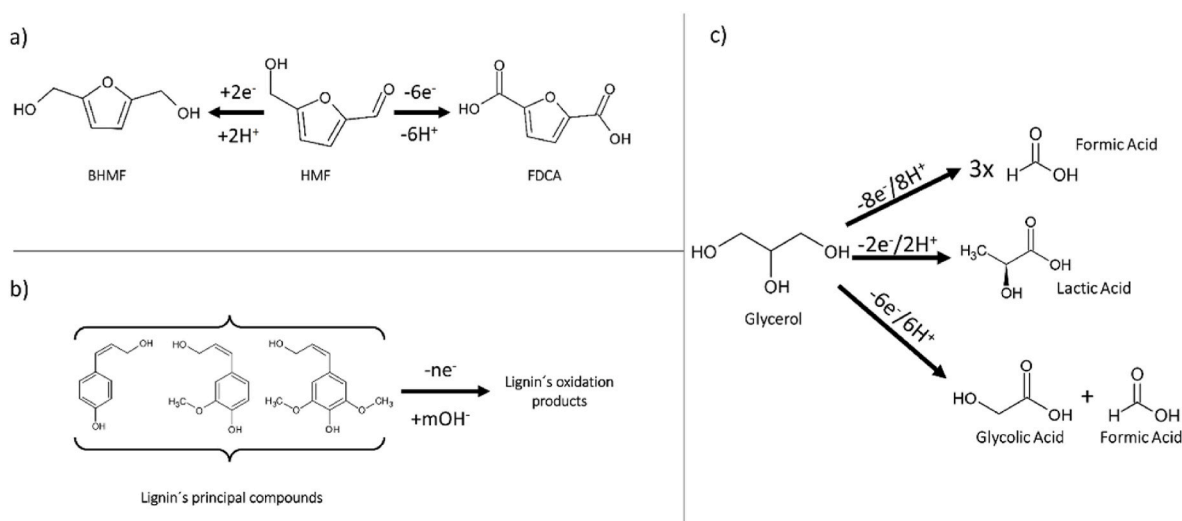


Fig. 1. Schematic representation of reactions for the valorization of a) 5-hydroxymethylfurfural, b) lignin and c) glycerol.

hydrogen source ( $H^+$ ) instead of  $H_2$  gas [34]. Besides, the energy necessary to start the process can be generated from renewable sources such as solar, wind, geothermal, reducing the use of energy derived from fossil sources [35].

The electrochemical oxidation of furanic compounds has extensively been studied in the literature at batch laboratory scale using metallic and metallic oxide electrodes [36], showing high yields and high faradaic efficiencies. Typically, Ni and nickel-based electrodes are employed for the oxidation of furfural and HMF, where the activation of the  $Ni^{2+}/Ni^{3+}$  ( $Ni(OH)_2/NiOOH^*$ ) redox pair is necessary [37]. To facilitate this activation, strong basic aqueous solutions are used and the oxidation of these molecules is achieved through successive Proton-Coupled Electron Transfer (PCET) reactions [38].

A two-compartment system with a three-electrode configuration is commonly used in batch for these reactions. The Nickel-based working electrode is placed in the same compartment as the reference electrode, while the counter electrode, usually made of Pt, is placed in the other compartment to prevent back reactions. Typically, initial concentrations of furan in the range of 10 mM and 1 M of metal hydroxide (e.g., potassium hydroxide, pH = 14) are selected for this reaction [32]. The challenge in using this condition is represented by the chemical instability of these compounds in strong basic media, which results in their degradation [39]. Performing the oxidation of HMF at pH < 14 leads to better results that could be considered for improving reaction conditions for a future scale-up of the process [40]. Generally, to obtain a high faradaic efficiency for the oxidation process, a potential range between 1.3 and 1.6 V vs RHE must be applied [41].

The use of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as homogeneous redox mediator in solution with a standard electrode, such as glassy carbon [42], or a semiconductor electrode, such as  $BiVO_4$  is helpful to promote the redox reaction  $TEMPO/TEMPO^+$  and, in turn, to achieve the HMF oxidation without requiring very high values of pH. With this methodology, it is possible to obtain high conversions of HMF and a high yield of FDCA at pH values in the range 7–9 [43].

For the electro-reduction reaction of HMF (and furfural), the best results have been obtained using Cu and CuAg alloy electrocatalysts [44, 45]. Starting from 20 mM HMF in borate buffer (pH = 9), the reduction (and hydrogenation) of the aldehyde group into an alcohol functional group [46] was performed with good results to produce BHMF employing potentials below  $-1.2$  V (vs Ag/AgCl) [47].

In a very recent work, Hauke and colleagues [48] explored the electrocatalytic reduction and valorization of HMF on novel noble metal-free Cu-based two-phase oxide precursor catalysts. The authors showcase the capability of oxide-derived Cu/MOx Cu foam electrodes to efficiently conduct the reduction of 5-Hydroxymethylfurfural to 5-Methylfurfuryl alcohol under alkaline conditions. This ability enables the effective operation of an alkaline exchange membrane electrolyzer, where the cathodic valorization of 5-Hydroxymethylfurfural is coupled either to alkaline oxygen evolution at the anode or to the oxidative valorization of 5-Hydroxymethylfurfural. Lignin depolymerization represents a highly favorable approach for the transformation of this polymer into high-value lignin-derived products. This method primarily involves the breakdown of the complex lignin macromolecule into smaller constituents utilizing a range of thermochemical routes, including pyrolysis, gasification, hydrogenolysis, oxidation, electrolysis, photocatalysis, and similar techniques. These processes aim to create smaller fragments that can be utilized in various applications, such as the production of fuels and chemicals [9]. Electrolysis holds a significant advantage due to its gentle operating conditions, including low temperature and pressure, which differ from traditional hydrolytic, thermolytic, and catalytic methods. Currently, much of the research involving lignin in electrolysis focuses on the direct production of green hydrogen. Nevertheless, lignin electrolysis also presents an opportunity to simultaneously generate valuable aromatic compounds, all while operating under milder conditions and with reduced energy costs compared to water hydrolysis [49]. Various electrochemical cell setups,

including 3-electrode cells, batch cells, and Polymer Electrolyte Membrane (PEM) reactors, have been employed in these processes. Multiple types of anodes, such as Pt, mild steel, Ni/C, Co/C, NiCo/C, Pt/C, and PtFe/C, and cathodes like Pt and mild steel, have been utilized [50,51].

A similar approach has been employed for the electrochemical oxidation of glycerol within an electrolysis setup. In an electrolyzer, the primary objective is to reduce the cell voltage to minimize the overall energy input, while still maintaining the necessary current densities for economically viable electrolysis. A strategy involves replacing the oxygen evolution reaction (OER) with the oxidation of organic molecules, such as glycerol. This substitution has the advantage of lowering the energy input due to the relatively lower oxidation potential of these organic compounds when compared to water [52,53]. By doing so, the process becomes more energy-efficient and economically viable. In literature, it has been reported a few methodologies where the concurrent generation of hydrogen or other products at the cathode is performed, while also producing valuable glycerol-derived products at the anode [10].

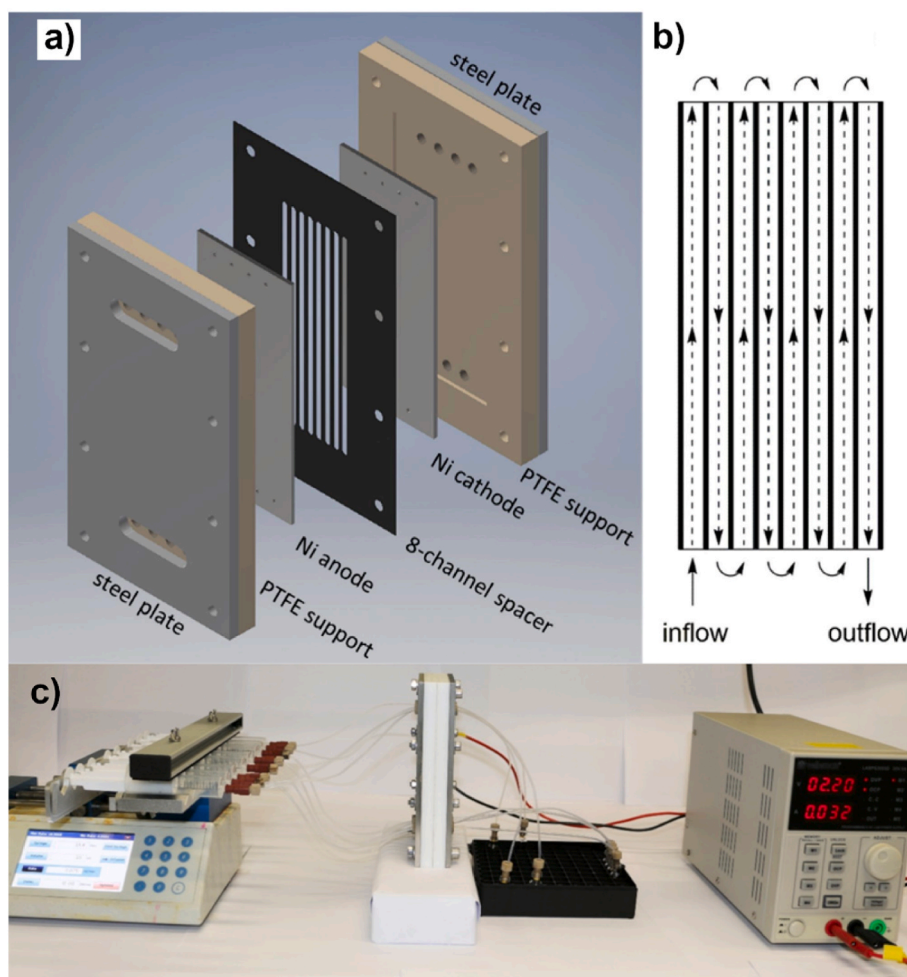
The production of these molecules presents many critical challenges when performed in batch. The integration of continuous flow technology with electrochemistry represents a powerful solution for facilitating the widespread adoption of large-scale electrosynthesis in industries. Flow electrosynthesis can effectively address challenges that commonly arise in conventional batch electro-organic systems, including issues related to mass transfer, ohmic drop, and selectivity [54]. Some authors have developed electrochemical flow cells for the valorization of biomass to take advantage of the improvements that a flow system can provide.

### 3. Continuous-flow processing applied to biomass valorization reactions

In the attempt of improving the efficiency of furanic derivatives production, different research groups have explored the use of continuous-flow reactors in HMF valorization. For example, Delparish et al. [55] reported the electro-oxidation reaction of HMF using an undivided flow-through microreactor with parallel plate electrodes made of Ni and a 8-channel spacer placed between them in order to provide a flow-pattern (Fig. 2a and b). The experiment was carried out in the potential range between 1.6 and 1.8 V (V Cell) with flow rate values from 0.1 to 4 mL/min and using increasing concentrations of HMF. The authors were able to perform the mass transfer characterization of the reactor by employing a model redox couple in order to obtain the mass transfer coefficient ( $k_{LS}$ ) and its relationship with the geometry of the reactor (area/volume ratio,  $a_{LS}$ ). Other important adimensional numbers, like Sherwood and Reynolds were also calculated, describing the ideal laminar flow regime.

Under optimized conditions, the HMF oxidation reaction showed a 97 % conversion of HMF and 87 % yield of FDCA at 1.7 V, at pH 13 and 0.1 mL/min, with around 100 % faradaic efficiency. However, the faradaic efficiency decreased below 50 % at 1.8 V due to the competition with the Oxygen Evolution Reaction (OER). The mass transfer limitations existing in the reactor were modelled based on experimental data. By means of a comparison between the faradaic current density data with the simulated current density, it was possible to interpret that only at low flow rates (<0.2 mL/min) and high potential values (>1.6 V), the HMF electro-oxidation reaction was mass transfer limited. At fast flow rates (>0.2 mL/min) and potentials higher than 1.8V, the system was dominated by kinetic limitations. Moreover, the relationship between the total product yields in function of the mass transfer coefficient ( $k_{LS}$ ,  $a_{LS}$ ) for this flow system, revealed that only through the improvement of the flow rate it was theoretically possible to increase the reaction yield.

In another example, Cao et al. [56] worked with a continuous multichannel flow electrochemical cell for the reduction of furfural to furfuryl alcohol (Fig. 2c). Interestingly, the authors were able to perform the reaction using only ethanol as a green solvent without the need for



**Fig. 2.** a) Schematic representation of the electrochemical parallel plate microreactor, b) flow-path in the reactor through the 8-channel spacer, c) continuous multichannel electrochemical flow reactor. Reproduced from Delparish et al. [55] under CC-BY license and from Cao et al. [56] under CC-BY-NC-ND license.

membrane separation or catalyst modification. The reduction was performed at ambient temperature and pressure in both acidic (potential of 2.90 V) and basic (potential of 2.20 V) conditions. In particular, the yield of furfuryl alcohol reached up to 90 % with a faradaic efficiency of 90 % in basic media, while in acidic conditions the yield decreased to 55 % with a faradaic efficiency of only 18 %. Interestingly, in basic conditions the reaction could be completed in only 10 min and required only a minimum amount of supporting electrolyte, highlighting the benefits of the microreactor.

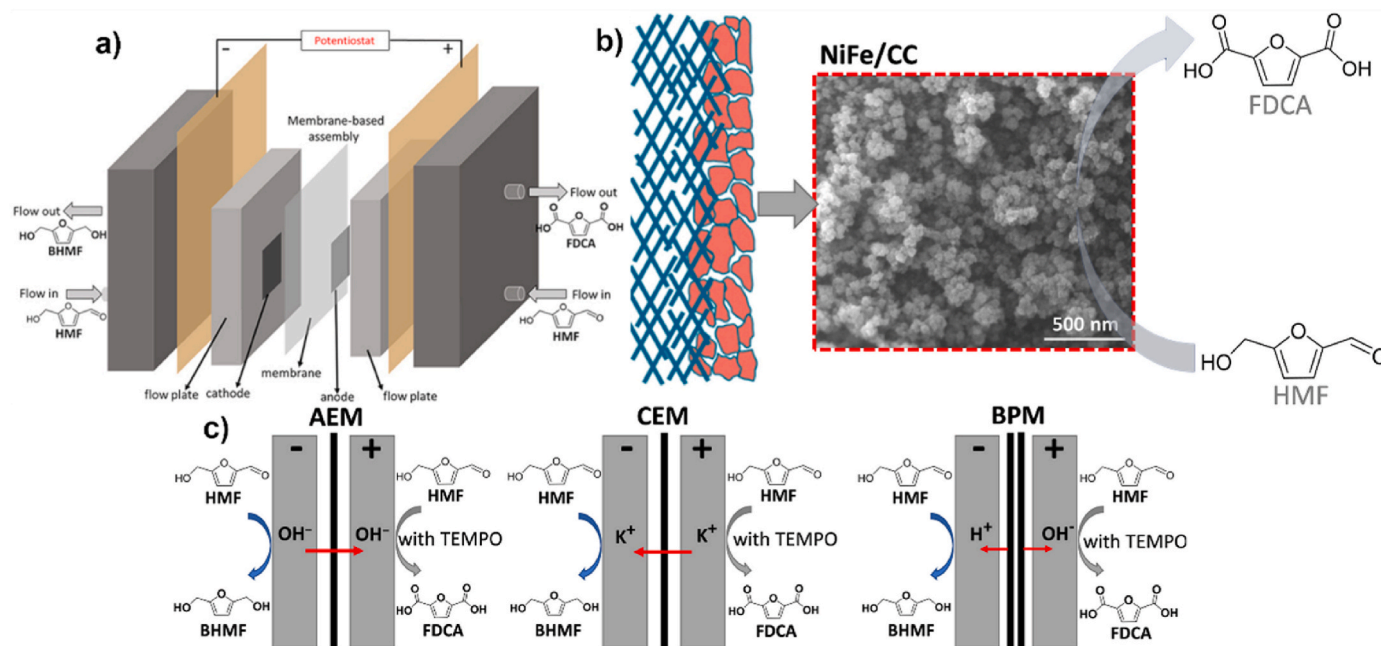
In another interesting work, Hauke et al. [57] presented a group of highly durable and selective catalysts, composed of interlayered bimetallic double-hydroxides containing nickel and another metal (iron, manganese, cobalt, or vanadium) with the interlayer spacing adjusted through anion exchange. This structural modification has led to significantly improved catalytic performance in the anodic production of FDCA, using a zero-gap MEA-type electrolyzer.

These examples consist of single pass flow regimes, but in some cases recycling the solution through the cell is an effective way to improve conversion, stability and current density [38]. For example, Liu et al. [4] showed a flow cell system with recirculation to obtain FDCA (at the anode) and BHMF (at the cathode) in a single cell (Fig. 3a and b). In this case, three different types of membranes were used to separate the two compartments: Anion Exchange Membrane (AEM), Cation Exchange Membrane (CEM) and Bipolar Membrane (BPM) (Fig. 3c). When using Ag nanoparticles (Ag NPs) as cathode and carbon cloth (CC) as anode in the presence of TEMPO as redox mediator, the system was stable for 24 h of electrolysis and displayed minimal cell voltage (1.5 V at 10 mA) with

AEM and CEM, while with BPM showed higher cell voltage (2.2 V) due to the higher membrane resistance and the additional voltage needed for water dissociation. A combined FE as high as 139 % towards BHMF and FDCA was achieved in the case of the AEM. When the system was employed in a pH-asymmetric configuration, and decorating the CC anode with NiFe, a similar high combined FE (125 %) was obtained without the need of the redox mediator. The same research group reported the utilization of an oxide-derived Ag electrode which demonstrated remarkable activity, achieving a 98.2 % selectivity in catalyzing the electrochemical hydrogenation of HMF into BHMF. This conversion process took place in a three-electrode flow cell. The researchers then explored an alternative approach, considering the oxidation of HMF to FDCA along with hydrogen generation as a more efficient alternative to the oxygen evolution reaction. When pairing the HMF-to-BHMF conversion with TEMPO-mediated HMF-to-FDCA conversion in the flow cell, a significant reduction in cell voltage, dropping from approximately 7.5 V to about 2.0 V, was observed when compared to the H-type cell. This resulted in more than a four-fold increase in energy efficiency during operation at 10 mA and a combined faradaic efficiency of 163 % was achieved for both BHMF and FDCA [58].

Other interesting examples that show how the implementation of a flow reactor electrochemical cells with recirculation improve biomass revalorization are Li et al. [59], Wang et al. [60,61], Diaz et al. [35], and Woo et al. [62]. In all these cases, high yields and faradaic efficiencies were obtained using high surface area electrodes.

Regarding the valorization of lignin biomass, Caravaca et al. demonstrated the production of pure H<sub>2</sub> via electrolysis of lignin



**Fig. 3.** a) Schematic illustration of the Membrane Electrode Assembly (MEA)-based flow electrolyzer, b) schematic illustration of the MEA-based flow electrolyzer with NiFe oxide electrocatalysts for oxidation of HMF and Ag NPs electrode for reduction of HMF, c) schematic illustration of the MEA configurations with different ion-selective membranes, including AEM, CEM, and BPM. Red arrows indicate the possible charge-carrying ionic species that transport across the membranes. Reproduced with permission from Liu et al. [4].

solutions in continuous-flow mode in a Polymer Electrolyte Membrane (PEM) reactor. In particular, the reactor employed Pt–Ru as catalyst at the anode and Pt/C at the cathode, while the polymeric membrane was made of Fumapen. The authors reported the production of  $H_2$  at the cathode at much lower electrical potentials (starting at  $\sim 0.45$  V) compared to conventional water electrolysis [63]. The same strategy was employed by Rodríguez-Fernández and colleagues that reported the production of  $H_2$  by water splitting with enhanced rates and efficiencies when using lignin as an additive in alkaline processes in the anode of an electrolyzer. The setup presented Ni foam for the cathodic reaction, whereas Pt/C and Pt–Ru/C nanoparticles were used as catalysts for the anodic counterpart. This approach demonstrated to be an effective way to avoid the rate-limiting Oxygen Evolution Reaction (OER) and to improve the performance of the AEM electrolyzer [64].

With respect to the electrochemical oxidation of glycerol, Tripathi and coworkers reported the synthesis of Co(II) doped  $Cu_2V_2O_7$  electrode assembly that could be used at both sides of a two-electrode electrolyzer as an efficient electrocatalyst for the oxidation of glycerol to generate formate along with the simultaneous production of  $H_2$  in alkaline water media [65]. In this dual-active catalytic process, the surface-immobilized catalyst demonstrates a performance with remarkably low overpotentials of 176 mV for the hydrogen evolution reaction and 160 mV for the glycerol oxidation reaction. In another interesting work, Vehrenberg et al. reported the successful coupling of the glycerol oxidation reaction at the anode to produce value added chemicals (formate, lactate and glycolate) with cathodic  $CO_2$  reduction to produce formate within a flow reactor, achieving a significant current density of  $50 \text{ mA/cm}^2$  [66]. Houache and colleagues demonstrated the use of carbon supported  $Ni_{0.9}Au_{0.1}$  catalyst for the electrooxidation of glycerol with 100 % selectivity toward formate and with 100 % conversion at +1.55 V. The co-electrolysis of  $CO_2$  and the glycerol process was performed, showing that the  $Ni_{0.9}Au_{0.1}/C$  catalyst attained the highest partial current density for CO of  $\sim 6.0 \text{ mA cm}^{-2}$  and the lowest onset cell voltage of  $-1.0$  V [67].

In the following section, the potential assets that 3DP reactors can provide in continuous-flow reaction will be showcased, focusing on

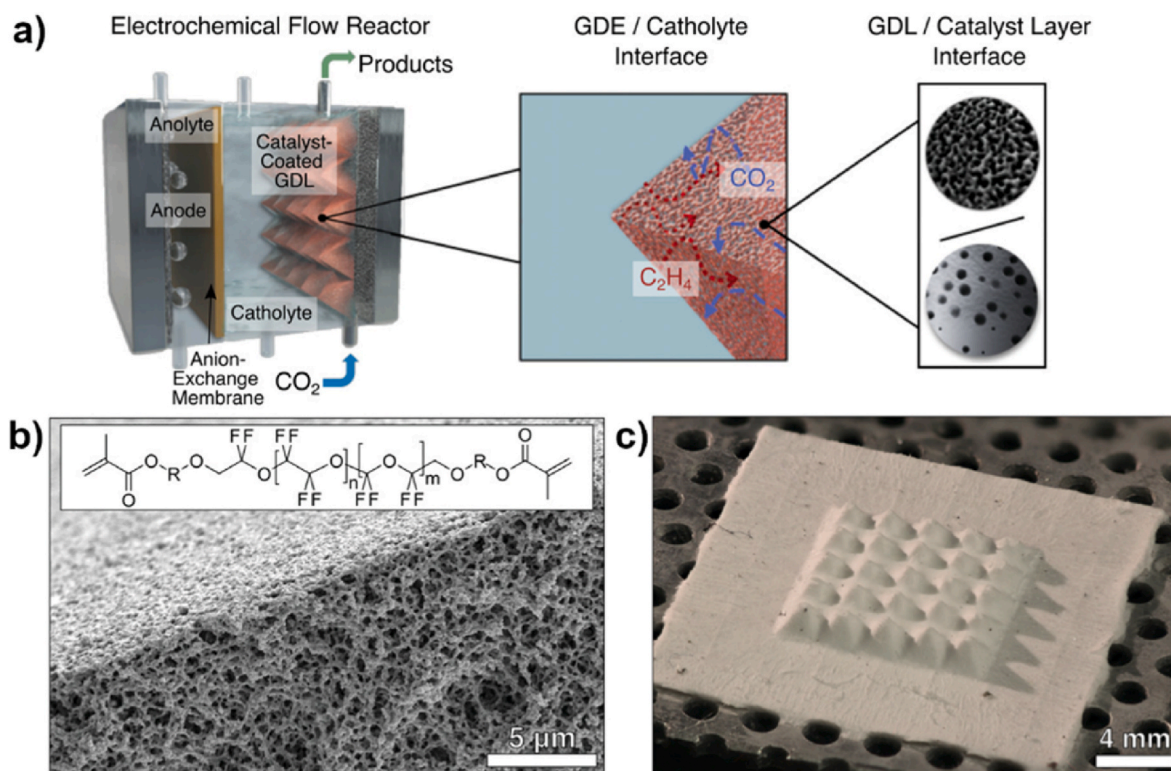
valuable examples of research groups that could benefit from the inherent flexibility in design which allowed for intricate and customized reactor geometries.

#### 4. 3D printed reactors

In the context of flow chemistry, 3D printed reactors provide several advantages compared to their non-3D printed counterparts, such as the possibility of incorporating intricate structures (microchannels and mixing elements), which can enhance mass and heat transfer, leading to improved overall reactor performance. Moreover, AM using metals and alloy allows the fabrication of objects with intricate geometry and exceptional durability, but at the same time it comes with higher costs, both in terms of materials and specialized equipment, and more complex post-processing requirements to achieve the desired surface finish and accuracy. On the other hand, polymeric 3D printing provides higher accessibility and versatility in material choices, ease of use, and rapid prototyping capabilities. Its limitations lie in low strength and heat resistance of the produced object compared to metals. Most components in a traditional flow cell can be fabricated via 3D printing thanks to the wide range of materials, including polymers (e.g.; polylactic acid (PLA), poly(propylene) or acrylonitrile butadiene styrene) which are widely used for the non-conductive parts such as the flow cell frame or turbulence promoters [68], and metals that can confer higher electrical conductivity, superior mechanical properties and better corrosion resistance, granting greater compatibility with diverse chemical reactions and harsh operating conditions [69].

An example is represented by the work of Marquez-Montes and colleagues that manufactured a filter-press electrochemical reactor in which different flow distributors and turbulence promoters were designed and manufactured by 3DP, displaying a suitable hydrodynamics and an enhanced mass transfer [71].

Wicks and coworkers reported the fabrication of a 3DP gas diffusion electrode for the electro-reduction of  $CO_2$  to value-added products (Fig. 4). The gas diffusion electrode was produced by photocurable perfluoropolyether monomers with tunable microporosity and high gas



**Fig. 4. Fluoropolymer Gas Diffusion Layers for CO<sub>2</sub> Electro-reduction.** a) Electrochemical flow cell with the 3D gas diffusion layer containing the copper nanoparticle catalyst (left); the macrostructure interface between the flowing catholyte and the gas diffusion electrode (middle); surface morphology at the GDL/catalyst interface (right). b) Homogeneous (H)-PFPE and c) large pore (LP)-PFPE. Reproduced with permission and adapted from Wicks et al., 2021 [70].

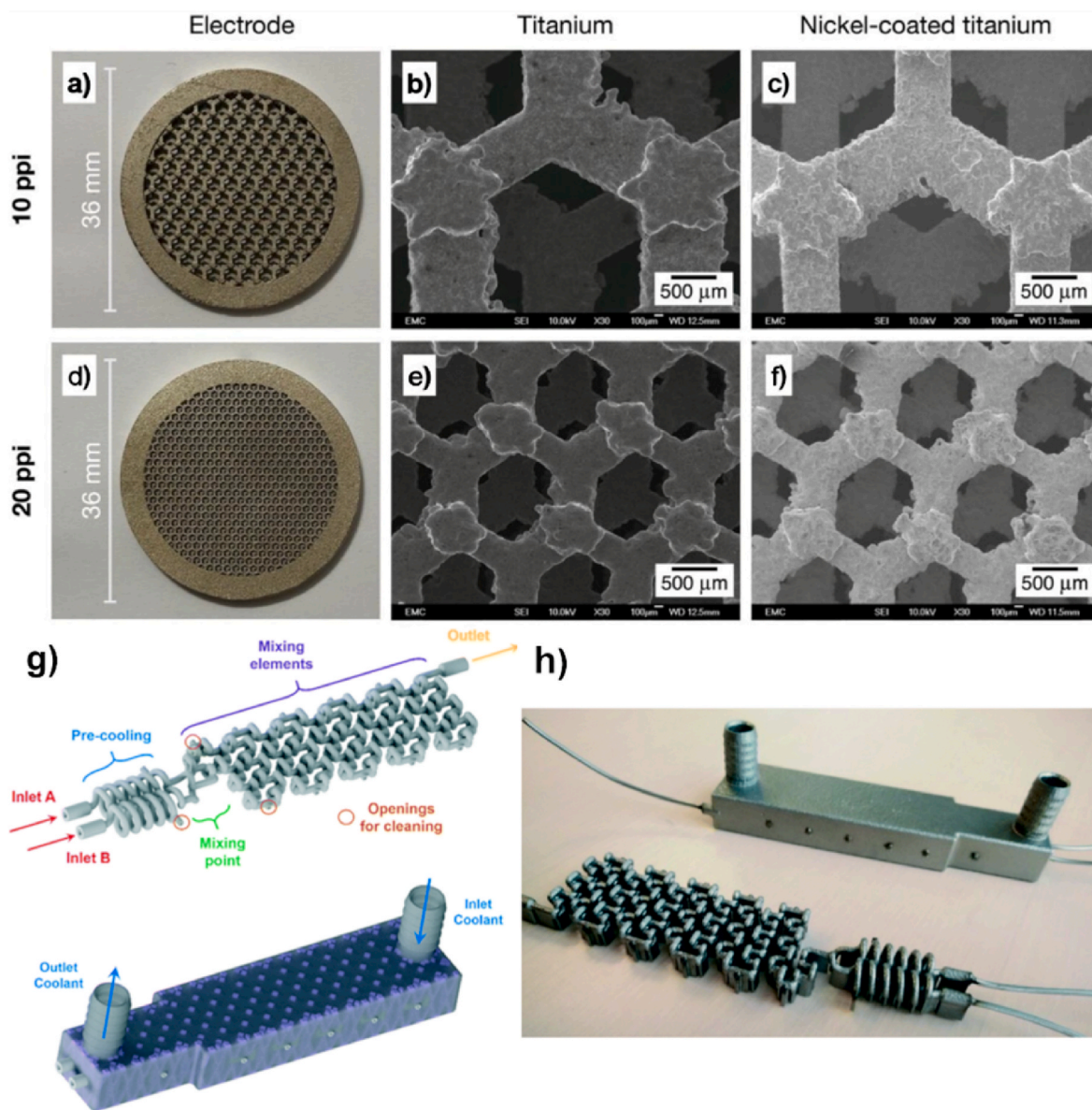
permeability, followed by the coating of a Cu catalyst layer. The authors demonstrated that the 3D structure morphology could shift the product selectivity towards C<sub>2+</sub> products, as a result of the gas transport [70]. In recent years, the fabrication of 3DP electrodes using fused deposition modelling has attracted great interest. Typically, conductive filaments composed of an insulating thermoplastic matrix and a conductive filler are used to produce electrodes that are then activated with organic solvents and/or high voltages to achieve electrochemically active materials [72]. By using the fused filament fabrication technique, Perales-Rondon and colleagues manufactured Cu-based electrodes from a Cu-containing filament. The electrode was used for nitrate-to-ammonia conversion, obtaining an impressive faradaic efficiency and high ammonia selectivity [73]. The same 3DP technology was used by Vaněčková and colleagues to manufacture electrodes from a conductive PLA/carbon black composite filament. The cylinder-shaped electrodes were finally activated by an electrochemical anodic procedure. Cyclic voltammetry investigations demonstrated that the faradaic peak separation values were superior to any values reported in literature for 3D printed PLA-based electrodes [74].

In most cases, polymers may be susceptible to degradation, particularly under harsh conditions [75], leading to several groups focusing their interest on laser power bed fusion techniques to 3D print components from stainless steel [69].

For example, Maier and co-workers reported a customized split and recombine reactor designed for the oxidation of Grignard reagents in flow (Fig. 5g and h). Moreover, the authors were able to integrate optical sensors for the inline monitoring of oxygen consumption in real time [77]. Arenas and colleagues reported the manufacturing of a porous electrode which could offer high volumetric area and enhanced mass transport properties. In particular, a highly ordered structure made of stainless steel was 3D printed and then coated with Nickel by electro-deposition in an acidic bath. The mass transport characteristics of this Ni/SS 3D-printed porous electrode compared well with and, in some

cases, even exceed those observed in typical planar, mesh and RVC electrodes [78]. The same group reported two other works where different materials were investigated for the production of the electrode by laser sintering and for the electrodeposition of the catalytic coating. In the first, an electrode with a titanium mesh presenting triangular pores was designed and manufactured by laser 3D printing using a powder fed device capable of 20 μm resolution, followed by the electrodeposition of a thin coating of platinum with strong adhesion. The resulting electrode could be suitable as a corrosion resistant anode for electrochemical synthesis [79]. In the second work, the authors described the fabrication of customized 3D flow-across electrodes that can maximize electrode-solution interaction and generate turbulence at the same time (Fig. 5a–f). In particular, they were able to fabricate nickel-coated titanium-alloy electrodes with different 3D porous architectures and with tuneable porosity by first manufacturing a 3D scaffold made of Ti-6Al-4 V alloy, and then the electrodeposition of the electrocatalyst was performed for applying the functional nickel coating [76]. A composite porosity electrode reported by Limper and colleagues was manufactured by selective laser sintering and could provide mass transport control inside of a reactor. In particular, the authors were able to produce a composite porous electrode with high surface area and passive mixing capability [80].

The intrinsic precision of 3DP allows for complex flow fields and multi-channel cell designs to target specific reaction requirements [81]. The impact of flow field pattern (serpentine, parallel, interdigitated, spiral, etc.) on reaction yields has been demonstrated, since it is straightforward to produce flow fields with multiple arrangements and exchange them within the cell [82]. In their work, Alvarez et al. [83] reported the fabrication of electrochemical continuous-flow oscillatory baffled reactors in which the combination of advanced mixing features with electrochemical transformations allowed to enable efficient electrochemical oxidations under continuous flow at a millimeter distance between electrodes. The reactor was manufactured employing different



**Fig. 5. Images of 3D-printed porous electrodes with hexagonal architecture:** a) Ti/Ni electrode with porosity grade 10 ppi, b) bare titanium alloy, c) nickel coated, d) Ti/Ni electrode with porosity grade 20 ppi, e) bare titanium alloy, f) nickel coated. Reproduced from Arenas et al. [76] is licensed under CC-BY-NC-ND 4.0. **Split and recombine reactor for the oxidation of Grignard reagents.** g) CAD drawings and h) 3D printed. Reproduced from Maier et al. [77] is licensed under CC-BY 3.0.

3DP technologies (*i.e.*, selective laser sintering and fused filament fabrication) and its enhanced performance was demonstrated in the oxidation of the cofactor NADH. In particular, the reactor design defined a pathway segmented by numerous baffles that under a continuous oscillatory flow promoted the generation of vortices, improving the mixing in the reactor and allowing for efficient anodic oxidation.

The use of AM to 3D print carbon aerogels has shown how this technology has the potential to impact several technologies [84]. These materials are unique porous solids with network structures consisting of interconnected carbon particles and, as a result, they exhibit many interesting properties, such as high surface-to-volume ratios, continuous porosities and high electrical conductivity. Recently, they have been reported as a major driver of innovation in the production of microbial electrochemical technologies (MET) by offering flexibility in complex and custom design of electrochemically active materials [85].

He and co-workers reported the fabrication of a hierarchical porous 3D-printed (3DP) graphene aerogel (GA)/polypyrrole (PPy) biocathode

(Fig. 6). This electrode was used for the conversion of  $\text{CO}_2$  to  $\text{CH}_4$  with an improved rate respect to carbon felt biocathodes. Its macroscopic interconnected pores allowed an enhanced mass transfer, while the microscopic pores offered a large specific surface area for microbial adhesion, displaying excellent biocompatibility [86]. Similarly, 3D printed carbon aerogel cathodes plated with nickel-molybdenum was reported by Kracke et al. for the production of  $\text{H}_2$  by MES [87].

## 5. Conclusions and perspectives

Additive manufacturing holds great potential for improving the performance of electrosynthesis processes. By leveraging the design flexibility and precision of 3D printing, customized electrodes, electrochemical cells (reactor) or reactor tools (*e.g.*, mixer or turbulence promoters) can be fabricated with enhanced features and capabilities. In Fig. 7, we summarize the state-of-the-art and some possible trends for the progress of this area.

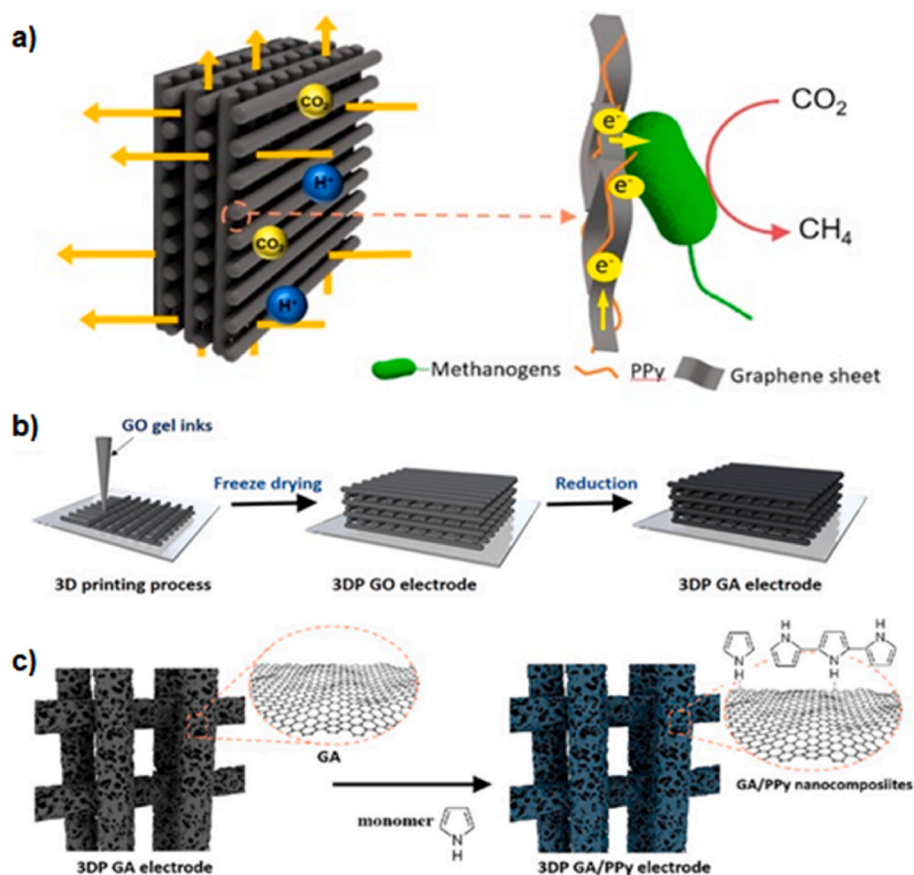


Fig. 6. 3D-printed GA/PPy aerogel biocathode. a) Schematic representation of the biocathodes. Schematic representation of b) 3D GA electrode preparation and c) polymerization of the 3D GA/PPy electrode. Reproduced and adapted with permission from He et al. [86].

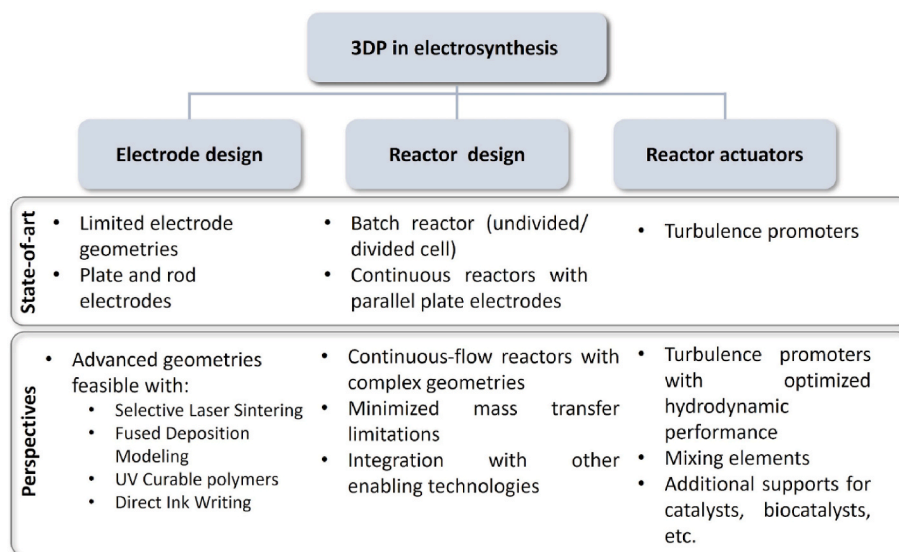


Fig. 7. Comparison between the state-of-the-art electrodes and reactors employed in electrosynthesis and the potential improvements that 3D printed elements can provide to enhance electrosynthesis performance.

Currently, it is common practice in electrosynthesis to employ round bar and plate electrodes for conducting reactions. However, these types of electrodes possess certain limitations, including a restricted active surface area for the reaction and the potential for performance degradation when the reaction product interacts with the electrode surface. On the other hand, the utilization of 3D printing technology in electrode

fabrication may offer a solution to these challenges. By employing 3D printing, porous electrode structures made of different materials can be created, effectively increasing the surface-to-volume ratio. This, in turn, enables a larger surface area for contact with the reagents, enhancing reaction efficiency and overall performance. Moreover, 3D printing allows for the integration of functional materials and catalysts into the



electrode design, enhancing selectivity, efficiency, and reaction kinetics.

The ability to rapidly prototype and iterate designs with 3D printing can enable researchers to explore and optimize reactor architectures for specific electrochemical reactions, leading to improved performance and greater control over reaction parameters. The tremendous potential of 3D printed reactors with complex geometries for electrosynthesis applications can allow for simple optimizations of mass transfer and heat transfer within the device. In fact, complex reactor designs can be created, incorporating features such as channels, baffles, turbulence promoters and split and recombine elements that would facilitate efficient mass transport of reactants and products, ensuring thorough mixing and reducing concentration gradients. Moreover, the optimization of heat transfer within the 3D printed reactor can enable precise control over temperature, promoting favorable reaction kinetics and minimizing side reactions. This combination of enhanced mass transfer and heat transfer capabilities in 3D printed reactors would allow for improved process efficiency and selectivity in electrosynthesis, making it an attractive and promising approach for achieving optimized electrochemical reactions. Moreover, combining 3D printing and fluid dynamics simulations (Computational Fluid Dynamics - CFD) can yield enhanced hydrodynamic performance in flow reactors. This synergy allows for the creation of custom-designed reactor components with intricate geometries, optimized flow channels, reduced pressure drop, and improved heat transfer capabilities. Furthermore, this approach offers flexibility in scaling, iterative design and testing, and the selection of materials suited to specific reaction requirements [88]. Ultimately, the integration of these technologies enables the development of highly efficient and tailored flow reactors, making it possible to achieve better mixing, precise temperature control, and improved overall chemical reaction outcomes.

During the last decade, 3D printing has been demonstrating to be a mature technology utilized as a toolkit for enhancing designs, optimize manufacturing processes, and create intricate and customized structures. Here, we showcased the assets that additive manufacturing can offer in terms of device optimization in order to improve the overall performance of electrochemical valorization of biomass substrates as an alternative and renewable source of useful products for the pharmaceutical, polymer and biofuel industries.

#### CRedit authorship contribution statement

**Gianluca Palmara:** Writing – original draft. **David Carvajal:** Writing – original draft. **Marcileia Zanatta:** Writing – original draft. **Elena Mas-Marza:** Conceptualization, Project administration, Fund raising. **Victor Sans:** Conceptualization, Project administration, Fund raising.

#### Declaration of competing interest

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

#### Data availability

No data was used for the research described in the article.

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