

Progress and roadmap for electro-privileged transformations of bio-derived molecules

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Cong Tian^{1,2,10}, Roham Dorakhan^{2,10}, Joshua Wicks^{2,10}, Zhu Chen²,
Kyoung-Shin Choi³, Nirala Singh⁴, Joshua A. Schaidle⁵,
Adam Holewinski⁶, Aleksandra Vojvodic⁷, Dionisios G. Vlachos⁸,
Linda J. Broadbelt⁹ & Edward H. Sargent^{1,2}✉

Biomass incorporates carbon captured from the atmosphere and can serve as a renewable feedstock for producing valuable chemicals and fuels. Here we look at how electrochemical approaches can impact biomass valorization, focusing on identifying chemical transformations that leverage renewable electricity and feedstocks to produce valorized products via electro-privileged transformations. First, we recommend that the field should explore widening the spectrum of platform chemicals derived from bio-feedstocks, thus offering pathways to molecules that have historically been derived from petroleum. Second, we identify opportunities in electrocatalytic production of energy-dense fuels from biomass that utilize water as the hydrogen source and renewable electricity as the driving force. Finally, we look at the potential in electrochemical depolymerization to preserve key functional groups in raw feedstocks that would otherwise be lost during harsh pre-treatments in traditional depolymerization routes. On the basis of these priorities, we suggest a roadmap for the integration of biomass and electrochemistry and offer milestones required to tap further into the potential of electrochemical biomass valorization.

Biomass represents a large source of already-fixed carbon that is globally available; its input, CO₂, has already been partially reduced via photosynthesis. Biomass is derived from diverse sources, including residue and biowaste from crops and algae. The estimated global supply of dry biomass from agriculture and forestry is approximately 12 Gt yr⁻¹, while waste biomass constitutes >100 Gt yr⁻¹ when one totals up industrial, municipal and food waste¹. Given its ~50 wt% carbon content², use of waste biomass fixes approximately -150 GtCO₂ yr⁻¹. The valorization of biomass holds potential in the sustainable production of biofuels, bio-based chemicals and biomaterials. One prominent application

is in the production of sustainable aviation fuels³, where a transition away from petrochemical feedstocks will contribute to reducing the carbon footprint of aviation.

We summarize the biomass processing landscape in Fig. 1a, rating feedstocks based on their H_{adj}/C ratio, where H_{adj} is the adjusted hydrogen content, representing the difference in the number of hydrogen and oxygen atoms, and also considering whether the feedstock is first generation versus second generation. We show different product categories along with processes used to obtain them and rank the process energy input (PEI) (for a detailed description of PEI scoring,

¹Department of Chemistry and Department of Electrical and Computer Engineering, Northwestern University, Evanston, IL, USA. ²Department of Electrical and Computer Engineering, University of Toronto, Toronto, Ontario, Canada. ³Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA. ⁴Department of Chemical Engineering, University of Michigan, Ann Arbor, MI, USA. ⁵Bioenergy Science and Technology Directorate, National Renewable Energy Laboratory, Golden, CO, USA. ⁶Department of Chemical and Biological Engineering, University of Colorado, Boulder, CO, USA. ⁷Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA, USA. ⁸Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE, USA. ⁹Department of Chemical and Biological Engineering, Northwestern University, Evanston, IL, USA. ¹⁰These authors contributed equally: Cong Tian, Roham Dorakhan, Joshua Wicks. ✉e-mail: ted.sargent@northwestern.edu

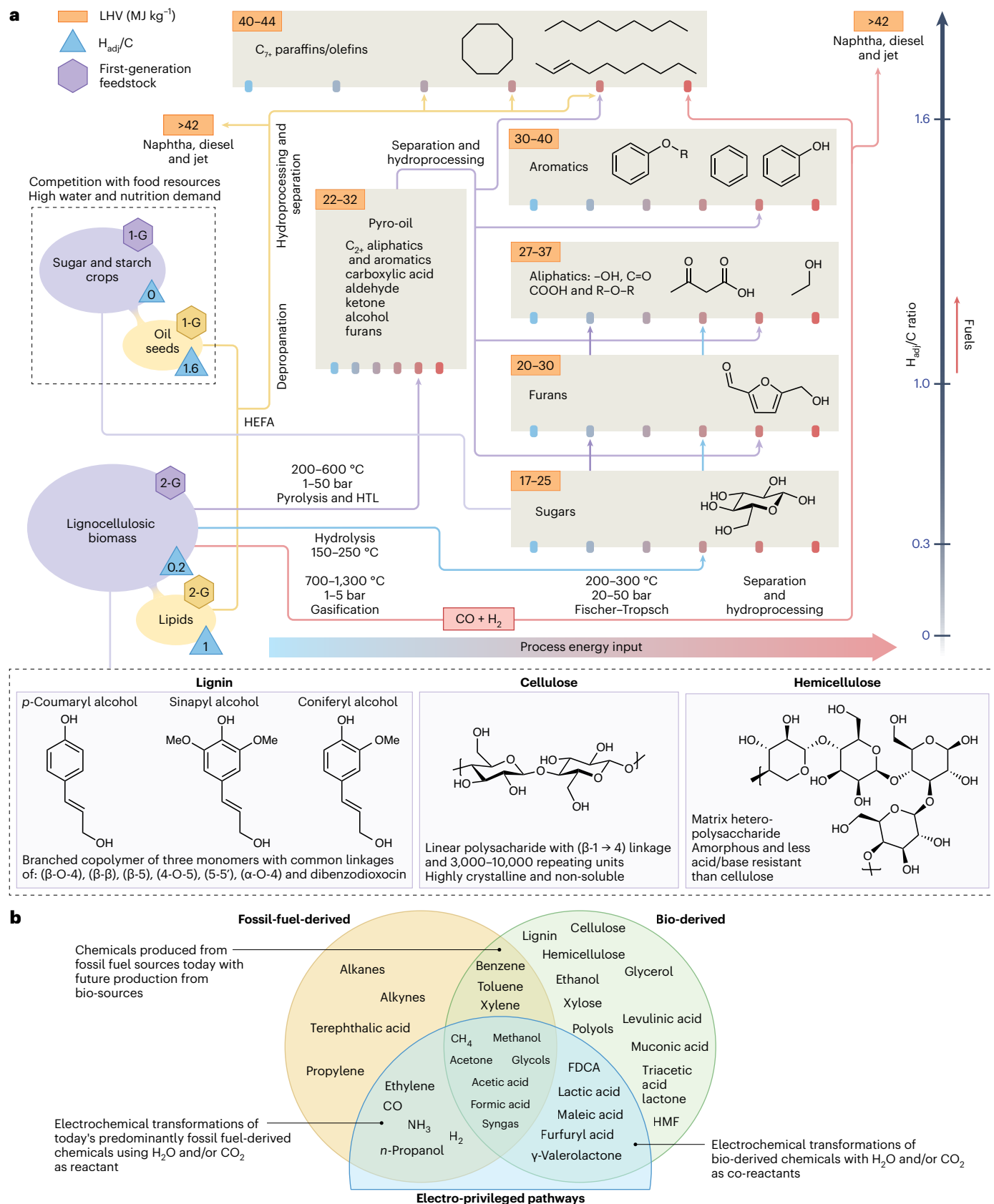


Fig. 1 | Process analysis for biomass valorization and electro-privileged transformation. **a**, The processing energy required in biomass chemical transformations varies significantly as a function of biomass feedstock and corresponding processes to achieve high energy density and H:C ratio in desired products. Multi-step reactions and harsh reaction conditions are needed and typically result in high overall energy input. The PEI values in this figure are

semi-quantitative and are based on processing temperature, pressure and separation energy (Supplementary Table 1). The legend includes the LHV of products (orange box), the H_{eff}/C value of feedstocks (blue triangle) and the type of feedstock (first (1-G) or second generation (2-G), purple hexagon). **b**, Interfacing electro-privileged pathways with present-day fossil fuel-derived and future bio-derived feedstocks and platform chemicals.

see Supplementary Table 1) required to produce each category using a given process. For example, lignocellulosic biomass feedstock (with an H_{adj}/C ratio of 0.2) can be used in a pyrolysis process to produce pyro-oil with a high PEI of 5–6. The pyro-oil product category has an H_{adj}/C range of -1–1.4 (the length of the product category along the y-axis) and can be converted to furans, short-chain aliphatics, benzylics and C_{7+} paraffins/olefins through hydroprocessing and corresponding separation. The product categories made through this route also have a significant PEI of 5–6, with C_{7+} paraffins/olefins having the highest H_{adj}/C ratios (>1.6), followed by aromatics, aliphatics and furans. Transformations with higher PEI have a higher energy demand and potentially higher carbon intensity associated with processing.

Today's biomass valorization landscape evidences a number of limitations. A first concern is that many biofuels today rely on first-generation edible feedstocks that may compete with food supply and may alter land use and increase food cost^{4,5}. To illustrate this, the production of approximately 42 million tons of bioethanol in the United States consumes 120 million tons of sugar- and starch-rich plants¹. Transitioning towards second-generation feedstocks such as lignocellulosic biomass seeks to address this issue; however, these feedstocks are today more energy intensive to process. This can be seen in Fig. 1a, where the production of furans, aliphatic and aromatics through pyrolysis, HTL (hydrothermal liquefaction) or hydroprocessing has a much higher PEI (5–6) when lignocellulosic biomass is used as the feed, compared with when sugar and starch crops are used. At present, their share in the biomass market remains small, with the contribution of lignocellulosic ethanol to total bioethanol production lying below 1% (ref. 5). The use of biomass-derived products will, in the long run, rely on the transition towards these second-generation feedstocks.

A second concern for existing biomass conversion processes (Fig. 1a) is their high PEI, linked to a demanding set of operating conditions in terms of temperature (as high as 1,300 °C in gasification)^{6,7} and pressure (ranging from 20 to 300 bar)^{8–11}. These necessitate specialized infrastructure and typically militate against a modular approach to plant design¹². Higher PEI also increases the carbon intensity of the product. This impacts both cradle-to-grave carbon intensity and cost.

These considerations motivate interest in alternative processes for biomass valorization, among which electrochemical processes^{13,14}—ideally ones that minimize energy consumption and contribute to decreasing overall carbon intensity—are candidates. Electrochemistry provides both oxidative and reductive chemical transformations¹⁵, each of interest in biomass processing¹⁶. Its reliance on increasingly available renewable electricity—expected to continue its growth and decline further in electricity's carbon intensity (CI, $\text{gCO}_2\text{e kWh}^{-1}$, gram of carbon dioxide emitted per kWh of electricity generated)—will create opportunities for lower-CI biomass-derived products. Precedents for scalable and industrialized electrochemical processes include the chloralkali process^{17,18} and, increasingly, green H_2 production, with electrification of biomass valorization remaining an open challenge and opportunity¹⁹.

In this Perspective, we define electro-privileged transformations of biomass-derived molecules (Fig. 1b) as those that utilize renewable electricity as a low-CI energy source, H_2O as hydrogen source and CO_2 as carbon source for hydrocarbon transformations; proceed under mild conditions that are suitable for modular deployment; and selectively produce the desired product range with minimal side reactions (electro-privileged molecules). We offer three priorities in biomass electrochemical valorization to meet the need for carbon- and energy-efficient production of chemicals and provide a roadmap for net-zero emissions that includes broadening the scope of biomass-derived feedstocks and electrochemically valorized products, identifying opportunities in electrochemical transformation of biomass to energy-dense fuels and pursuing direct electrochemical depolymerization of raw biomass feedstocks.

Rapid progress in a set of electrified transformations of biomass platform chemicals

Biomass platform chemicals²⁰ are building blocks produced by biomass pre-treatment that are ready for further valorization. In contrast to the case of fossil fuel-derived chemicals, oxygen-containing functional groups naturally formed in biomass can be preserved in these molecules, eliminating the need for downstream oxidation processes²¹. The aromaticity of molecules in lignin can be preserved, removing the need for processes such as the aromatic catalytic reforming of naphtha employed on petroleum feedstocks²². Similarly, amino groups found in biomass can be preserved in platform chemicals, thus circumventing downstream amination processes.

Electrochemical approaches can offer mild reaction conditions with oxidation and reduction potentials and electrolytes finely tuned to oxidize or reduce only a desired functional group. This includes the selective oxidation of only a secondary alcohol of polyols (for example, glycerol)²³, the preferential oxidization of an alcohol group instead of an aldehyde group (or vice versa)²⁴ and the oxidization of an alcohol group to only an aldehyde group without further oxidizing to a carboxylic group²⁵. The reductive valorization of aromatic molecules and unsaturated hydrocarbons presents opportunities for electrochemical reduction towards fuels, fuel additives and other hydrocarbon products²⁶. Both electrochemical oxidative and reductive conversion of these biomass platform chemicals can retain desirable functional groups while modifying the chemical structure to obtain diverse downstream products with high selectivity. A range of electrochemical biomass platform chemical valorization pathways published in the last decade are mapped in Fig. 2a.

When evaluating candidate chemicals, we look at three groups of biomass-derived feedstocks: bio-alcohols (glycerol and ethanol), bio-acids (formic acid and levulinic acid) and furans (5-hydroxymethylfurfural (HMF) and furfurals). Each class of platform chemical has a variety of valuable derivatives with large and growing markets (Fig. 2b). Valorization of these platform chemicals could lead to products that serve as drop-in replacements for petrochemicals or might instead replace them with chemicals that can be further processed to provide similarly useful physical and chemical properties. Certain chemicals can be obtained through electrochemical transformations with high selectivity, energy efficiency and reaction rate; such biomass-derived products are referred to as electro-privileged.

Glycerol, a by-product of biodiesel with multiple hydroxyl functional groups, can be oxidatively upgraded to valuable chemicals²³ having market sizes larger than that of glycerol. Electro-oxidation of glycerol produces a range of carboxylic acids, ketones and aldehydes that can be used as C_1 – C_3 feedstocks in polymers, medicines and food^{27,28}. Mechanistic studies²⁹ of glycerol oxidation assisted by in situ spectroscopy reveal the stabilization of certain reaction intermediates and deprotonation during C–C cleavage as critical steps influencing product selectivity. Hence, discriminative stabilization of certain intermediates and controlling deprotonation kinetics can help enhance product selectivity.

HMF is considered to be a versatile biomass platform chemical owing to its multi-functional groups capable of oxidative upgrading towards various products. HMF is potentially also an electro-privileged molecule owing to a reduction of the carbon footprint using electrochemical processing steps. The electro-oxidation of HMF to 2,5-furandicarboxylic acid (FDCA) has attracted attention as a biomass-derived replacement for terephthalic acid (TPA) in producing commercial polymers³⁰. Employing wind-generated electricity, FDCA could reach a carbon footprint of as low as 0.3 kgCO_2 per kg of FDCA³¹, while TPA suffers from a cradle-to-gate carbon footprint of 2.6 kgCO_2 per kg of TPA.

Furfural has also been examined as a biomass-derived building block inclined to both oxidative and reductive valorizing transformations³². Furfuryl alcohol and furoic acid are some of the

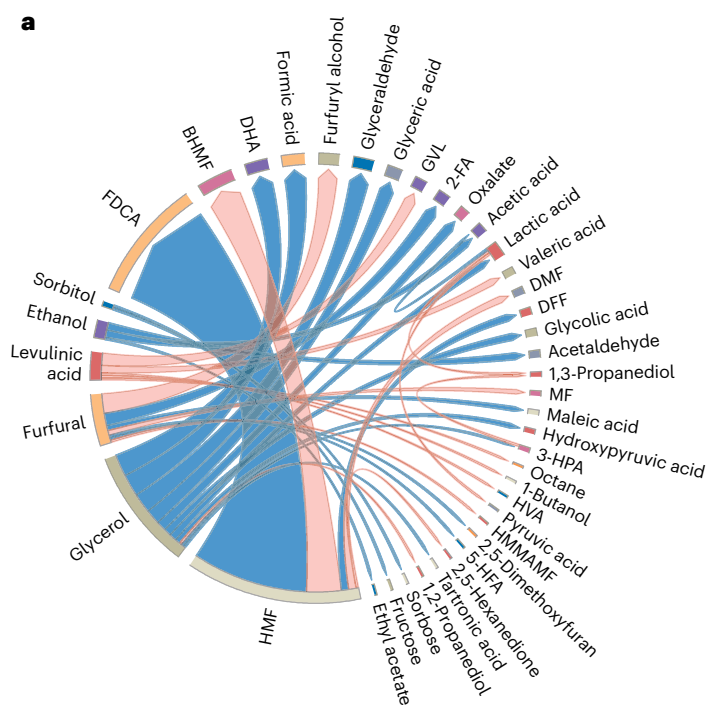


Fig. 2 | An overview of certain electrochemical biomass valorization studies reported in the past decade. **a**, Reduction reactions (red) and oxidation reactions (blue), where the direction of the arrow indicates reactant to product, including dihydroxyacetone (DHA), γ -valerolactone (GVL), 2-furoic acid (2-FA), 2,5-diformylfuran (DFF), 2,5-bis(hydroxymethyl)furan (BHMF), 2-methylfuran (MF), 3-hydroxypropionic acid (3-HPA), 4-hydroxyvaleric acid (HVA), 2,5-dimethylfuran (DMF), 2-hydroxymethyl-5-(methylaminomethyl)furan (HMMAMF) and 5-hydroxyfuroic acid (5-HFA). The size of the label corresponds to the number of reports out of the total of 132 publications. Details of the

b

Reactant	Product	FE (%)	Total current density (mA cm ⁻²)	Today's market size of product (US\$)	Reactant global production volume (tonnes per year)	Product global production volume (tonnes per year)
Bio-ethanol	Acetic acid	100	598	20 billion	86 million	20 million
Lactic acid	Propylene glycol	0.002	4	4.3 billion	1.4 million	1.9 million
HMF	FDCA	100	200	441 million	NA	82 million ^a
Furfural	Furfuryl alcohol	89	50	473 million	0.3 million	0.2 million
Glycerol	L-lactic acid	72	570	2.9 billion	2.8 million	1.4 million
Glycerol	Formic acid	99	10	1.8 billion	2.8 million	0.7 million

publications are provided in Supplementary Table 2. **b**, Bio-derived precursors and potential products via electrocatalytic upgrading. Ethanol is a promising bio-derived precursor for chemical manufacture owing to its high global production volume, whereas increased lactic acid production would enable access to the large propylene glycol market using electrochemistry. HMF, furfurals and glycerol are the most researched biomass-derived chemicals in electrochemistry owing to the large market size and their application potential. ^aProduction volume of terephthalic acid, which can be replaced by FDCA. NA, not applicable; FE, Faradaic efficiency.

products accessible from furfural³³, of interest for their application in furan resins and FDCA^{34,35}, respectively. Recent works have studied the pH-dependent selectivity shift between furfural alcohol and 2-methylfuran, as well as the benefit of aqueous-organic co-solvents to inhibit side-production of humins³⁶.

Lignin monomers represent a variety of oxygenated molecules generated from lignin depolymerization². These renewable aromatic feedstocks can be unstable owing to the presence of unsaturated oxygenates such as alkenyl, aldehydes, ketones and carboxylic acids and need further valorization before use as fuels and chemicals. Electrocatalytic hydrogenation (ECH) offers mild reaction pathways to produce diverse chemicals including phenol, guaiacol, syringol and cyclohexane³⁷.

Broadening the scope of valorization of biomass-derived platform chemicals

In light of these examples of progress in electrified biomass valorization, we recommend that the field further widen the spectrum of electrochemically valorized chemicals, which should encompass diversity in both biomass-derived reactants and products. We provide examples of how diversity in feedstock and/or product range can be achieved.

Bio-ethanol is widely used as a fuel additive^{4,38}, used as a drop-in fuel, owing to its high energy density and availability, in internal combustion engines and fuel cells, with the latter attracting much interest in recent years³⁹. Bio-ethanol also provides a suitable platform (when sourced from non-edible lignocellulosic feedstocks) for the production of chemicals⁴⁰. We recommend a further focus on the electrochemical valorization of bio-ethanol into acetic acid⁴¹, a commodity chemical with applications in paints, adhesives and plastics⁴², having a market

size of US\$20 billion per year and 86 million tonnes per year (Fig. 2b). Its volume is comparable to that of bio-ethanol, today coming from fossil fuel-derived methanol and carbon monoxide through carbonylation routes.

HMF is one of the most versatile platform chemicals, being able to serve a variety of products through oxidative and reductive treatments. However, it has mostly been the object of research for electrochemical transformation to FDCA (Fig. 2a). We recommend focusing on its upgrading intermediates and processes to control and diversify electrochemical products. For example, by leveraging operando spectroscopies and quantum mechanical simulations^{24,30,43}, researchers have gained mechanistic insight into the electro-oxidation of HMF: key intermediates of 2,5-diformylfuran and 5-hydroxymethylfuran-2-carboxylic acid have been identified, and mechanisms have been proposed including hydrogen atom transfer (HAT) and hydride transfer⁴⁴. These insights assist in developing catalysts and systems that target non-FDCA products and diversify the product range of HMF feedstocks⁴⁵.

Levulinic acid, a C₅ bio-acid formed by cellulose hydrolysis⁴⁶, can be valorized to valeric acid, γ -valerolactone and 4-hydroxyvaleric acid (a precursor to biodegradable polyhydroxyalkanoates) via electrochemical reduction reactions⁴⁷. Recently, neo acids, a new class of platform chemicals conventionally produced from petroleum-derived olefins, have been synthesized from biomass-derived levulinic acid via hydroxyalkylation/alkylation and further hydrodeoxygenation (HDO)⁴⁸. We suggest the development of a tandem system that integrates thermocatalytic hydroxyalkylation and ECH reactions to produce the desired neo acids.

Exploring electro-privileged transformations does come with challenges specific to electrochemistry. Most biomass-derived

feedstocks contain multiple functional groups, some of which need to be selectively targeted during oxidation/reduction, without other groups being affected. The advance in cell design enables efficient selectivity control, especially in single-pass biomass conversion with concentrated feedstocks⁴⁹. Operating at sufficient current densities is of importance to minimize capital expenditure. However, the high voltages applied to generate sufficiently high current densities may result in overoxidation of the feedstock to CO₂ and an increase in competing oxygen evolution reactions during electro-oxidation as well as the hydrogen evolution reaction (HER) in the case of reduction. In case of reduction reactions, a suitable complementary oxidation reaction must be identified to mitigate the need for a high-voltage oxygen evolution reaction or sacrificial anodes, whereas oxidation reactions can be paired with the HER to simultaneously produce green hydrogen. These challenges motivate opportunities to focus on: sequential oxidation–reduction reactions in one-cell electrochemical reactors, the study of reaction mechanisms by theoretical and spectroscopic techniques, surface engineering for novel and efficient/selective heterogeneous catalysts, and electrolyser design as a means to minimize side reactions.

Electroreduction of biomass-derived feedstocks produces energy-dense hydrocarbons

Biomass-derived fuels (biofuels) such as bio-ethanol and biodiesel are already being deployed as low-carbon transportation fuels and additives^{38,50}. Biofuels require high energy density to offset their production cost and become feasible fuels. The drawbacks associated with the distributed nature of biomass feedstocks and the transportation costs will be lower per unit energy for biofuels that are higher in energy density and manufactured close to their source.

Energy-dense hydrocarbons require a high H:C ratio with a low O:C ratio²⁶. Traditionally, this has called for transforming oxygenated biomass-derived feedstocks using thermochemical processes to increase the H_{adj}/C ratio (Fig. 1a). The transformations constitute both the removal of oxygen atoms and the addition of hydrogen atoms, through HDO, increasing the H_{adj}/C ratio and the overall energy density of the molecule. Hydrogenation involves the addition of hydrogen atoms to increase the saturation of C–C or C–O bonds. HDO can constitute the cleavage of C–O bonds and the formation of C–H bonds through (1) hydrogenolysis, (2) decarbonylation/decarboxylation or (3) dehydration to form unsaturated C–C bonds. We term the electrochemical counterparts of hydrogenation as ECH, the hydrogenolysis category of HDO is termed electrocatalytic hydrogenolysis (ECHy) while the other categories of HDO (2 and 3) are termed electrocatalytic deoxygenation (ECDO). The target product range of these processes should possess an H_{adj}/C ratio >1 and a lower heating value (LHV) >30 MJ kg⁻¹. This highlights the importance of aromatics, aliphatic and C₇₊ paraffins/olefins as important target fuels.

High-carbon (C₈–C₂₂) alkanes in the jet/diesel range can be synthesized from lignocellulosic biomass via C–C coupling of monomers followed by HDO to increase their LHV⁵¹. Various coupling reactions of biomass-derived furans, including hydroxyalkylation, alkylation and aldol condensation, can deliver high yields of long-chain hydrocarbons that are suitable for fuels, lubricants and detergents⁵². However, HDO reactions typically require harsh reaction conditions that lead to high energy consumption and undesirable C–C cleavage. Therefore, electrochemical reduction reactions hold potential to replace HDO and produce similar high-carbon biofuels.

Biomass gasification followed by Fischer–Tropsch and hydroprocessing allows access to energy-dense product streams, at the expense of high PEI attributed to harsh gasification conditions⁵³. Hydrolysis offers a lower-PEI option; however, the corresponding products have lower energy density. Pyrolysis and hydrothermal liquefaction can be performed in milder conditions than gasification, but the significant separation cost of the resulting complex pyro-oil mixture has limited its techno-economic feasibility to date. Hydroprocessed esters and fatty

acids are a low-PEI alternative, but they are limited to oil seeds and other lipid-rich feedstocks, the former a first-generation feedstock competing with food resources. All these reactions require access to considerable H₂ as reductant and suffer from its associated carbon footprint and energy cost, depending on the production method. The reaction conditions of these processes suggest the potential to scale economically, while the distributed nature of second-generation biomass feedstocks is slated to benefit from modular transformation processes.

Water-based electrolytes, as a proton source, lead to the HER as a side reaction, requiring dedicated catalyst design to suppress the HER and enhance selective ECH without reducing its efficiency. Although H₂ may prove useful in biomass conversion processes, having careful control over the selectivity of ECH is important for energy efficiency. An understanding of what materials or sites catalyse ECH or HER is needed. As an example, for Pt and Rh, the terrace sites are active for ECH of phenol⁵⁴ while step sites are not, so using electrocatalysts with a higher fraction of terrace sites increases the selectivity to ECH.

A challenge for reductively upgrading biomass—compared with the reduction of water, CO₂ or N₂—originates from the fact that biomass-derived molecules often have multiple functional groups that can be reduced. Each functional group may undergo reduction reactions mentioned above (1–3) in a competitive manner. Thus, selectively reducing only a specific functional group, and to a prescribed degree, is critical to obtain a desired product with high selectivity. Electrochemical approaches combine a tunable applied potential with a bespoke electrolyte composition (pH, with specific cations and anions to regulate the reduction mechanism). Mechanisms specific to electrochemical reduction may further offer pathways to increase the diversity of and selectivity to products. For example, the hydrogenation of an aldehyde group to an alcohol group is not an initial step of the hydrogenolysis of the aldehyde group to an alkane. Instead, the hydrogenation of the aldehyde group and the hydrogenolysis of the aldehyde group are competing reactions, preferring different hydrogenation mechanisms. This means that both the alcohol product and the alkane product can be obtained with high selectivity by electrochemically controlling the competing mechanisms under ambient conditions.

Understanding the reaction mechanism through a combination of spectroscopy and kinetic studies⁵⁵, including studying the effect of reaction conditions on activity and selectivity⁵⁶, is foundational to pursuing such electrochemically orthogonal reaction pathways as well as for designing more active catalysts and reaction conditions for each pathway. Another potential method to control selectivity is using temperature. Although most studies for ECH are done at room temperature, there can be benefits to operating at different temperatures, such as increasing the temperature to increase the catalyst activity or controlling the temperature to promote desired over undesired reactions. For typical electrochemical reactors that use polymer exchange membranes (for example, Nafion), the reaction temperature can readily be increased up to 80 °C.

Understanding the impact of electrocatalytic conditions such as temperature and voltage on catalyst lifetime is essential owing to potential deactivation issues in biomass mixtures. While ECH operates at lower temperatures than thermocatalytic hydrogenation, it can encounter problems such as deactivation from by-product build-up⁵⁷, or the applied potential may induce catalyst dissolution. By comprehending these deactivation modes and testing various mechanisms, the catalyst stability can be enhanced. Electrocatalysis also offers methods to control deactivation. Adjusting the temperature or the electrochemical potential can protect catalysts from poisoning and reduce leaching⁵⁸, thereby extending the electrocatalyst lifespan.

Energy-efficient thermo- and electro-pathways for the transformation of biomass to fuels

The feasibility of ECH, ECHy and ECDO have been demonstrated using certain biomass platform chemicals as feedstock^{44,59}. Current studies

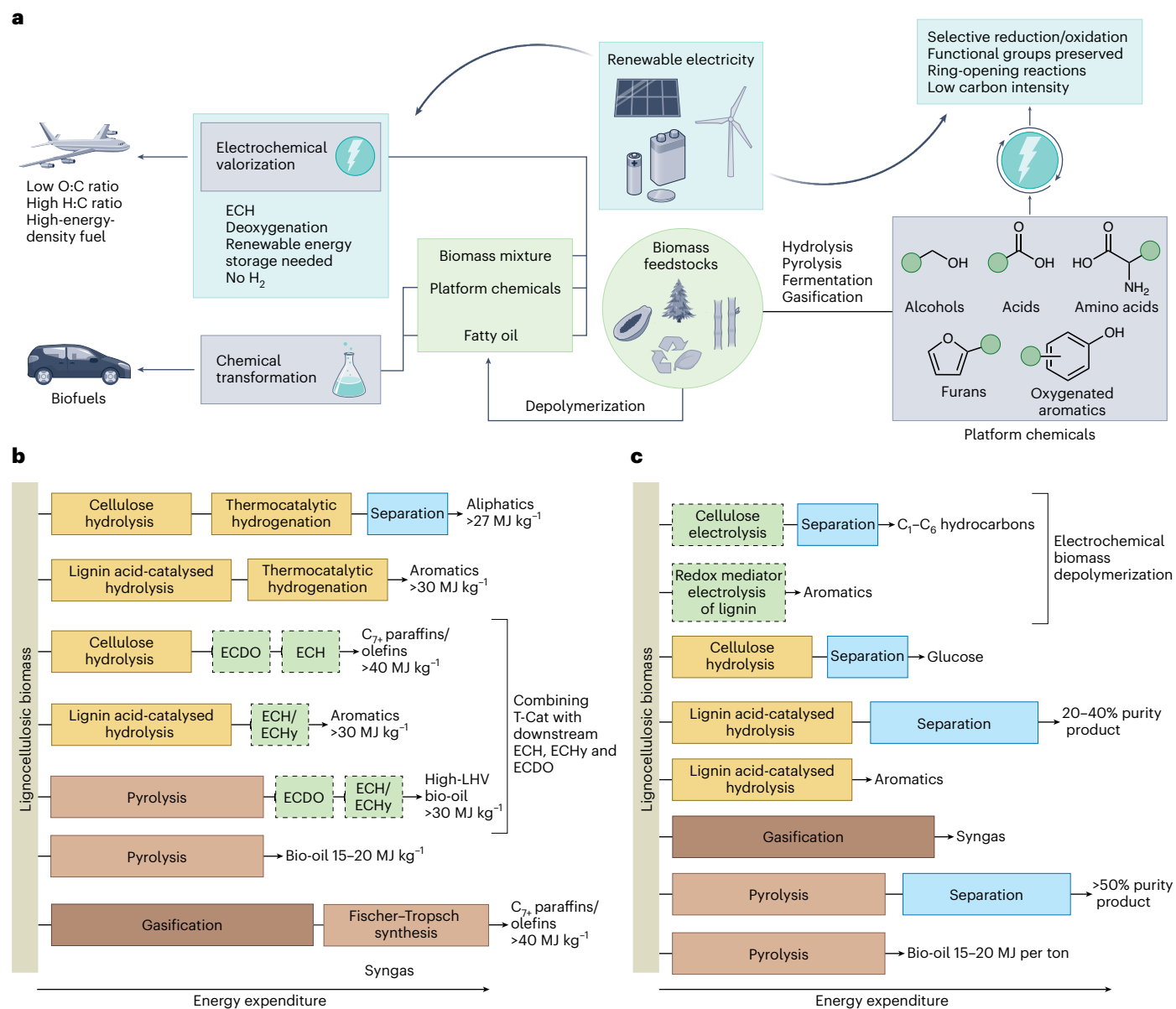


Fig. 3 | Electrochemical biomass valorization pathways. **a**, Electro-privileged valorization starts from electrochemical feedstock depolymerization to fuels that store renewable energy and to valorized chemicals via biomass platform chemicals. **b**, The energy expenditure of conventional pathways and electrochemical alternatives in biomass valorization for fuel production. The length of each box corresponds to its energy expenditure. Yellow, low-energy

thermochemical processes, for example, cellulose hydrolysis; light brown, higher-energy thermochemical processes, for example, pyrolysis; dark brown, the most energy intensive thermochemical processes, for example, gasification; green, electrochemical processes, for example, ECH; blue, separation processes. T-Cat, thermocatalysis. **c**, The energy expenditure of conventional pathways and electrochemical alternatives in cellulose and lignin depolymerization.

focus on the transformation of single platform chemicals into more hydrogenated forms.

We propose to expand the feedstock list of ECH, ECHy and ECDO to encompass not only platform chemicals but also low/mid-PEI chemical mixtures that suffer from low H_{adj}/C ratios, for example, pyro-oil and sugar/furan mixtures from cellulose hydrolysis (Fig. 1a). These mixtures would be ideal targets for low-PEI electrochemical reduction reactions such as ECH, ECHy and ECDO, forming a low-PEI and low-CI biomass transformation network to increase the product H_{adj}/C ratio and produce fuels. The modularity of electrochemical systems, their independence from pressurized hydrogen gas and their ability to controllably hydrogenate mixture feedstocks make them an ideal technology for biofuel production and rendering the fuels generated via this method electro-privileged products. The chemical variety present in feedstock

mixtures poses a challenge for catalyst and system design, a challenge that requires progress in materials synthesis, separation and reaction engineering. We thus highlight the importance of exploring mixtures as feedstocks, where potentially a sequence of ECDO, ECHy and ECH is needed in a specific order to enable the production of a fuel with high H_{adj}/C ratio. An example would be the reduction of HMF, where although the feedstock is not mixed, reaction conditions can facilitate either ECH, ECHy or both, depending on the reaction pH^{44,60}. This also highlights the importance of site-specific ECDO strategies, which could cleave ECHy-susceptible oxygen species before ECH, eliminating ECHy side products.

Another avenue is the exploration of a wider product range from platform chemical reduction. Opportunities exist where competing reactions that produce multiple products, each with moderate

Biomass processing	Demonstrating feasible depolymerization of any one biomass polymer via electrochemistry	Demonstrating depolymerization for example, a cellulose, hemicellulose or lignin	Modular and energy-efficient electro-privileged pathways displace a portion of thermochemical depolymerization processes
Low-carbon biofuels	Improving efficiency of electrocatalytic hydrogenation Coupling biofuel production with anodic upgrading reactions	Electro-privileged biofuels achieve an LHV >42 MJ kg ⁻¹	All biofuels contribute 3,300 TWh of energy globally in the IEA's net-zero emissions scenario
Valorization of platform biomolecules	Broad portfolio of products from platform biomolecules Highly selective transformations enabled by electro-privileged pathways	Development of a pilot-scale biorefinery	Electro-privileged bio-derived molecules reduce demand for fossil fuels as chemical feedstocks
	Phase I	Phase II	Meeting net-zero emissions goals by 2050

Fig. 4 | Roadmap to contribute to net zero. A roadmap charting the development of electro-privileged biomass transformations across three pillars: biomass processing, low-carbon biofuels and the valorization of platform biomolecules. IEA, International Energy Agency.

H_{adj}/C ratio, can have their products co-reacted to produce a unified product stream with higher H_{adj}/C ratio and energy density. Cellulose and hemicellulose-derived bio-acids such as lactic acid and levulinic acid can be converted to fuel-grade long-chain alkanes and cycloalkanes with high energy density using ECH. There, the myriad of products, each not a suitable fuel, can be cross-reacted with each other to produce octane, a valuable and energy-dense fuel. This inspires the study of side reactions and potential opportunities to produce product mixtures that can be transformed to energy dense fuels with a low-PEI thermo/electrochemical process. These recommendations are summarized in Fig. 3b, where the sequential combination of thermochemical biomass treatment with downstream ECH, ECDO and ECHy can lead to products with higher energy densities with lower energy expenditure.

Advancements in electrochemical reduction reactions will require deepened understanding of mechanistic pathways. Clarifying the reaction mechanism can direct catalyst and system design to achieve those goals. In the case of ECH reactions, there are key differences between electrochemical pathways and their thermocatalytic counterparts. Unlike thermocatalytic hydrogenation processes that rely on H–H cleavage in H_2 , ECH can utilize H_2O directly to produce adsorbed hydrogen (H^*) or drive direct proton-coupled electron transfer from the solution^{60–62}. ECH reactions have been demonstrated for the transformation of biomass platform chemicals to fuels²⁶ and can benefit from better PEI than thermocatalytic alternatives. We recommend a focus on three additional mechanistic questions with particular relevance to the ECH of biomass species. What catalysts and reaction conditions achieve selective ECH while minimizing other competing reduction reactions (for example, ECDO and ECHy)? How do interactions between the different molecules in biomass mixtures affect their conversion through ECH? What are the mechanisms of catalyst deactivation in the conversion of biomass products? ECH and ECHy are known to be competitive in nature, requiring careful control over reaction environment to selectively produce ECH or ECHy products. The diverse pool of molecules and functional groups present in ECH gives rise to intricate interactions that complicate conversion prediction. While competitive adsorption between reactants is common^{63,64}, conditions sometimes favour faster ECH rates for mixed molecules,

hinting at enhanced conversion possibilities^{65,66}. Identifying conditions where mixtures may enhance conversion is a potential opportunity for ECH. An implication of the difficulty of converting biomass mixtures is that it is unclear whether the best process will use a single type of catalyst that converts multiple molecules effectively or a diverse set of catalysts that can convert different types of molecules. Identifying which route is preferred will require an improved understanding of ECH in these mixed streams.

In addition to direct ECH, ECHy or ECDO for fuel production, electrocatalysis can assist in processing steps that are upstream or downstream of the reduction process. CO_2 can be a common by-product in biomass transformation and may be directly converted to energy-dense hydrocarbons by using CO_2 electroreduction systems that have been well developed during the past decade^{13,67}. Biogas, another chemical stream available in biomass processing units containing mainly CO_2 and methane⁶⁸, can be utilized for electrochemical reduction to synthetic natural gas and other chemicals for further upgrading. Lastly, SO_x and NO_x impurities produced during biomass gasification can be removed by selective reduction or oxidation using electrocatalytic systems⁶⁹.

Existing pre-treatment strategies for the exploitation of lignocellulosic biomass

Lignocellulose, regardless of source, can—in contrast to the case of starch—be diverted for chemical and fuel production without affecting nutrition supplies and act as a carbon-neutral feedstock for replacing fossil fuel-derived chemicals⁷⁰. However, owing to its complex chemical structure, strong hydrogen bonds and resistance to solvents, lignocellulosic feedstocks require harsh pre-treatments such as enzymatic catalysis, pyrolysis, gasification or hydrolysis before being upgrading to useful intermediates and building block chemicals, hindering their broad utilization as feedstocks⁷¹. Lignin depolymerization can occur through reductive and/or oxidative cleavage of C–O and C–C bonds across monomeric groups, preserving aromatic functional groups⁷². In nature, this is done via oxidative and hydrogenative enzymes⁷³ designed to drive enzymatic lignin depolymerization. In industry, the processing of biopolymers is mostly done through thermochemical methods such as pyrolysis and gasification, where thermal energy is used to cleave

bonds non-selectively, or oxidize them via addition of an oxidizing agent, for example, O₂ (ref. 74). Cellulose depolymerization is markedly less energy intensive through hydrolysis, but upstream separation of lignin from cellulose in lignocellulosic feeds adds to the energy cost of the processes. There is a need for strategies that can process lignocellulosic biomass efficiently, ideally without the need for upstream lignin separation, and utilize the lignin for chemical production.

Enzymes, mostly from bacterial and fungal species, have been used for catalytic lignin depolymerization owing to their mild reaction conditions and high product selectivity. However, enzymatic degradation generates large amounts of CO₂, releasing the bio-immobilized carbon and reducing the overall carbon utilization. However, the high-temperature conditions required for pyrolysis lead to poor selectivity, producing a wide range of products that raise the separation costs. Specifically, catalytic pyrolysis induces radical formation and, in turn, eliminates many desired functional groups. Gasification⁷⁵ eliminates all functional groups, making for a circuitous production path via syngas, which will inevitably suffer from high energy costs and low overall energy efficiency. This low energy efficiency also reduces the net energy gain from downstream fuel synthesis processes. High temperatures are necessary in both pre-treatment and the process itself, including devolatilization and gasification of the produced char at 700–1,300 °C. Hydrolysis processes⁴⁶ are energy intensive and destroy valuable functional groups contained in the feedstock. Moreover, most thermal hydrolysis processes require strong acids and harsh reaction conditions, making the process and acid recovery economically unfeasible.

Electrifying the depolymerization of raw biomass feedstocks

Electrochemistry⁷⁶ offers a route to pre-treat lignocellulosic feedstocks under mild conditions (Fig. 3c). Particularly when lignin-derived chemicals are used, electrochemical depolymerization can proceed at the anode to deliver various bio-acids, which preserves valuable carboxylic groups, or at the cathode to conduct selective reductive C–C cleavage in lignin linkages⁷⁶. One way to understand the mechanism of electrochemical depolymerization in lignocellulosic feedstocks is to study the degradation of lignin fragment dimers, as the selective cleavage of linkages is critical to understanding how to preserve valuable benzene rings and functional groups⁷⁷. Aromatic monomers, including phenol, guaiacol and syringol, can be obtained via ECH of lignin dimers, with various reports indicating mixed product distributions using single-metal catalyst materials. Moreover, the tunable oxidative or reductive capacity of electrochemistry through voltage control can potentially be used to selectively treat cellulose and lignin in mixed lignocellulosic feedstocks, alleviating the need for costly upstream separation of the two.

Challenges^{78–80} remain in the evolving field of electrocatalytic lignin depolymerization. Reactants can be subjected to overoxidation in the electrochemical system and lead to undesired CO₂. Biopolymers may not easily dissolve; the limited interaction between the electrode surface and polymers restricts the reactivity. Reactants can be subjected to overoxidation in the electrochemical system and lead to undesired CO₂. Thus, optimizing the pH and identifying an appropriate co-solvent that can maximize the solubility of the biopolymers without affecting the rate of oxidation and product selectivity are needed. Designing electrochemical reactors that overcome the issues with the restricted interaction between the polymer structure and the electrode and overoxidation are essential. For example, a recently reported electrochemical membrane reactor⁷⁹ expels chopped-off depolymerized fragments from the anolyte. This can help the core portion of the biopolymer come into contact with the electrode surface more frequently. The depolymerized fragments are removed from the anolyte, so they cannot undergo overoxidation before the depolymerization of the core part is completed. When such or further improved reactor

designs (that is, reactors that can allow cascade reactions) are coupled with new electrocatalysts that can achieve selective depolymerization, based on the strategies developed for other electrocatalytic reactions such as alloying and catalyst surface modification, interesting new opportunities will emerge for the selective depolymerization of raw biomass feedstocks to useful chemicals.

Another strategy that can be used to address the restricted interaction between the polymer structure and the electrode is to use redox mediators^{78,81}, which allow the depolymerization of biopolymers without them directly contacting the electrode. Product selectivities achieved by the use of redox mediators can be different from those obtained by heterogeneous catalytic electrodes, increasing the product diversity. For the practical use of redox mediators, the synthesis of robust, inexpensive and easy-to-recover mediators may be needed, depending on the reaction conditions and the desired product type with the customized design of reactors for the oxidation and recovery steps.

Outlook

The decreasing carbon intensity of electricity provides avenues to pair electrochemistry with biomass-derived feedstocks. However, electrochemical biomass valorization has largely been limited, until now, to fundamental studies. In Fig. 4, we summarize milestones along which the union of electrochemistry and biomass valorization can contribute to net-zero decarbonization goals. Phase I aims to highlight the near-term accomplishment of each priority pathway, phase II maps to a corresponding deliverable that signals the translation of research into industrial application, and phase III describes the way in which each priority contributes to our outcome of net zero in 2050. Comprehensive research, including aspects from electrochemistry, materials science and systems engineering, will be needed to address the challenges above.

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Author contributions

E.H.S. supervised the project. C.T., R.D., J.W. and E.H.S. co-wrote the paper. All authors discussed the ideas and assisted during the preparation of the paper.

Competing interests

The authors declare no competing interests.

Additional information

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Correspondence should be addressed to Edward H. Sargent.

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