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Anode co-valorization for scalable and sustainable electrolysis†

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Increasingly abundant and low-cost renewable electricity is driving the fast development of electrolysis for energy storage and CO_2 valorization. However, current electrolyzers rely on the oxygen evolution reaction (OER), which has been expensive, location limited, high-risk, and generates low value (O_2) recovery. In this perspective review, we analyzed the state-of-the-art in electrolysis processes that use alternative anode reactions to improve the economic viability and scalability of water or CO_2 electrolysis. We quantitatively compared a wide range of inorganic and organic electron donors in the anode that can lower energy costs and/or produce value-added products, and then assessed the use of different biotic and abiotic catalysts and the feasibility of using low-grade water sources as electrolytes. Through this wide-ranging assessment, we developed an example study for large-scale electrolysis in California, USA, provided long-term perspectives on OER substitutes for anode co-valorization, and delivered insight on future research directions.

1. Introduction

Renewable power has become increasingly cheap and abundant, enabling large-scale electrolysis and carbon valorization.[1,2] In countries such as Germany, the United States, Canada, Brazil, and Mexico on-shore wind power has been distributed at levelized costs as low as 3 cents per kW h,[3] and due to fluctuating supply and demand, wholesale electricity prices have even temporarily become negative.[4,5]

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Recognizing this as an energy storage challenge and opportunity, such low-priced renewable power can seamlessly be upgraded to renewable fuels and products by electrochemical water or CO_2 reduction (CO_2-R), supporting zero emission goals and a circular carbon economy.[6,7] Such devices simultaneously tackle the United Nations Sustainable Development Goal (SDG) 7 on Clean Energy and SDG 13 on Climate Action,[8] yielding tremendous societal benefits.

However, in order for these new technologies to obtain a meaningful market share, costs must be minimized to become competitive with current production methods. Hydrogen (H_2) produced from electrochemical water reduction comprises only 4% of the global market[9] and it was recently indicated that the costs need to be decrease by an additional $0.80 per kg to become economically practical *versus* industrial-scale steam reforming.[10] Likewise, the cost of electrochemical CO_2 reduction products will need to be priced at an aggressive $1 per gasoline gallon equivalent to be on-par with alternative fuels that satisfy the US Department of Energy (DOE) biofuel production goals for 2020.[11]

Electrolysis typically involves two half reactions, an oxidation reaction on the anode and a reduction reaction on the cathode (*i.e.* H_2 evolution or CO_2 reduction). To date, many researchers have focused on improving reduction efficiencies and expanding the portfolio of products that can be generated at the cathode[12] while the equally important anode reactions have not received the same attention nor have attained the same rate of improvement. State-of-the-art electrolyzers still rely on anodic O_2 evolution reactions (OERs, eqn (1)) to provide electrons and charge balancing ions from water.[13]

$$2H_2O \rightarrow 4H^+ + 4e^- + O_2 \tag{1}$$

Though convenient, the OER is unsustainable, requires expensive catalysts, generates a low-value product (*i.e.* O_2), and demands high amounts of energy to overcome the thermodynamic barrier that drags the scalability of the whole system. For instance, Kenis *et al.* (2019) recently found that the OER typically consumes around 90% of the total electricity input to CO_2 electrolyzers.[14] In addition, the OER can have a large potable water footprint[15] and creates chances for dangerous gas mixtures (*e.g.* O_2/H_2) to form if not operated properly.[16]

In light of these limitations, several OER alternatives have been proposed to decrease energy consumption and/or generate high-value products that can offset operation costs and improve sustainability [Fig. 1]. These reactions can tackle a range of objectives including raw chemical generation (*e.g.* H_2O_2), waste oxidation, and molecule upgrade. By coupling worthwhile oxidation reactions at the anode with cathode electrosynthesis, industries can leverage existing infrastructure for purification, distribution, and waste-management, and even produce feedstock chemicals required for parallel processes housed at the same facility. Employing such co-valorization tactics can indeed address current drawbacks of the OER by increasing revenues and the value proposition of the overall process.

OER alternatives can be initiated by thermochemical,[17] photochemical,[18] electrochemical,[19] and biological processes,[20] with the latter two being the most mature. For instance, the industrial-scale chloroalkali process substitutes the OER for sodium chloride (NaCl) oxidation at the anode while electrochemically generating H_2 at the cathode.[21] With many possible OER replacements, primary considerations can focus on the anode operating potential and market value of the products. Hereto are described many organic and inorganic reactions that can be operated at much lower potentials than the OER, greatly decreasing energy inputs [Fig. 1]. For instance, the oxidation of a waste product, urea, can take place at a standard potential of just 70 mV,[22] potentially reducing energy demands by 94% *vs.* OER (calc. in S2†). On the other hand, some reactions can generate products valuable enough to justify higher operating potentials than the OER.

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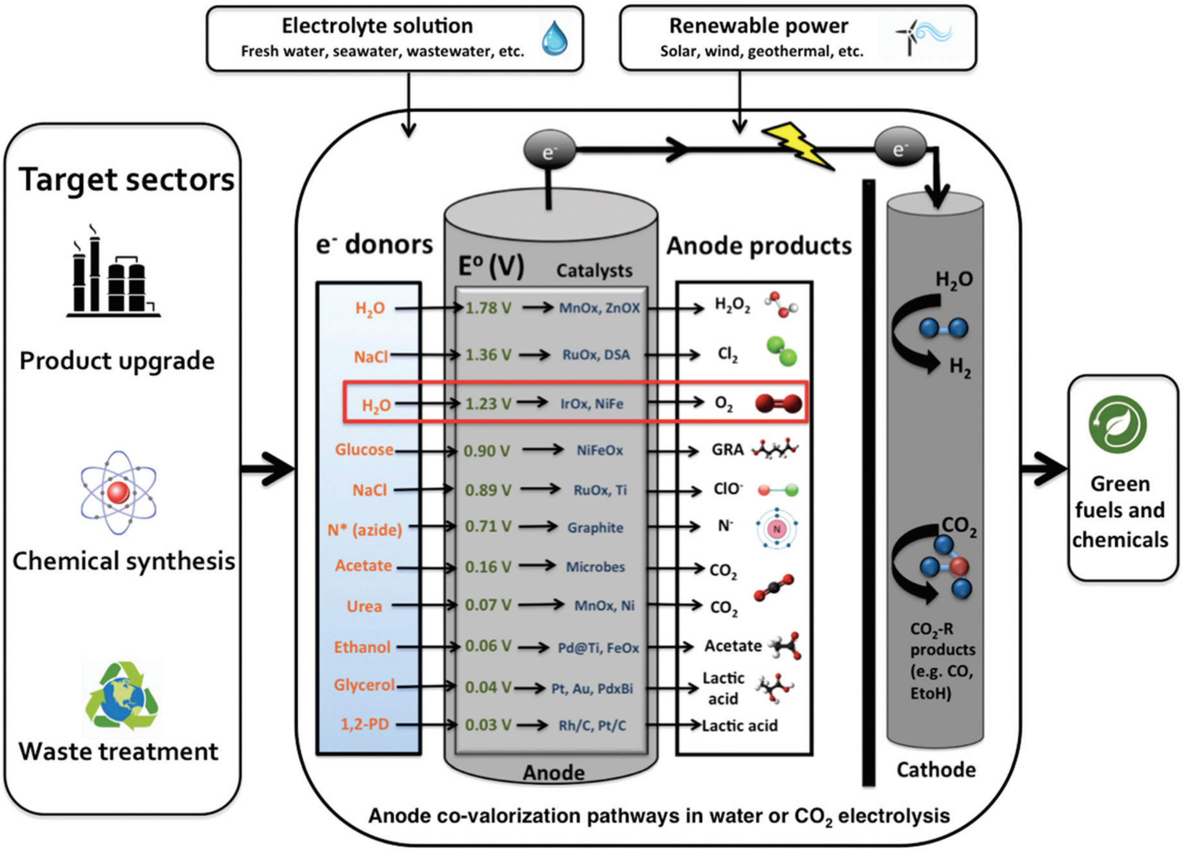

Fig. 1 Different anode co-valorization pathways in electrochemical water or CO_2 electrolysis. The combination of electron donor, catalyst, and products are summarized for each co-valorization option, and related industries and benefits are illustrated; summary of standard redox potentials of OER and substitutes reactions *vs.* Reversible hydrogen electrode (RHE). Acronyms defined in Table S1† [ref. 22 and 24–37].

For example, the standard redox potential of H_2O_2 production (*via* H_2O oxidation) is around 30% greater than the OER, but the market value of H_2O_2 is about 23 times greater than O_2.[23] Still, OER substitutes should preferably be operated with low-energy inputs and generate high-value products. Ancillary considerations should be that the target anode products are non-corrosive to catalysts, easily separated from solutions, resistant to cross-over to the cathode, and do not form hazardous product mixtures. Additionally, feedstock reactants should be inexpensive, plentiful, and complementary to cathode electrosynthesis.

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In practice, it may be difficult to find a reasonable OER substitute that meets all these criteria so a secondary method to lower OER expenses could be to reduce the costs of the electrolyte. The OER typically uses a high-purity water electrolyte, similar to standard potable water that is currently priced around \$3.38 $kGal^{-1}$.[38] Owing to growing water scarcity, water rates have been steadily increasing (3.6% APC)[38] and in areas like El Paso, Texas have surged by over 33% in a single year.[39] To bypass these costs, the use of inexpensive and abundant impaired water sources should be considered for the OER and alternative anode reactions. Impaired waters can include any body of water that doesn't meet one or more regulatory water quality standards that comprise it's designated use.[40] The US alone generates 34 billion gallons of wastewater per day,[20,41] which could be a cheap and readily available source of low-grade water. Recently, pilot-scale microbial electrolysis (MEC) systems have been demonstrated that utilize microbes at the anode to oxidize organics in wastewater (around 1 V below OER), providing electrons for H_2 production at the cathode while also reducing the costs of wastewater treatment.[42] Similarly, inland surface water and groundwater, as well as seawater (that covers 70% of earth[43]) are also viable water-electrolyte sources. In fact, many have investigated the use of seawater as an electrolyte for water reduction[44] but catalyst degradation and chloride oxidation have been major hurdles.[45]

In this perspective review, we discuss various co-valorization tactics to improve the economic viability and sustainability of scalable water or CO_2 electrolysis. We consider a wide range of inorganic and organic reactions that can lower energy costs and/or produce value-added products. We also compare the use of biotic *vs.* abiotic catalysts, and examine the feasibility of using low-grade water sources as electrolytes. Through this wide-ranging assessment, we develop a case study for large-scale electrolysis in California, USA and provide long-term perspective on OER substitutes that delivers insight on future research areas.

2. Co-valorization reactions on the anode to replace the OER

2.1. Inorganic oxidations

Inorganic molecule oxidations are an attractive route to replace the OER as they often utilize low-value feedstock and do not produce CO_2 as a by-product. Fig. 2 includes the applied potentials of 6 inorganic reactions at peak selectivity and their performance in coupled water reduction and electrochemical CO_2-R systems. The feasibility of such designs has been confirmed by industrial-scale electrolysis platforms like the chloro-alkali process that uses NaCl to generate chlorine gas (Cl_2) and hypochlorite (NaClO) at the anode while generating H_2 at the cathode.[46] Such devices offer a useful roadmap to bring substitute OER reactions to the commercial-scale.

Fig. 2a shows that NaCl oxidations have reached some of the highest faradaic efficiencies (FEs) amongst prospective OER substitutes. Recently, some have used catalysts like ruthenium oxide coated titanium (RuO_2/Ti) to achieve excellent anodic conversions (FE 99%, 1.5 V) of NaCl to ClO^- while redu-

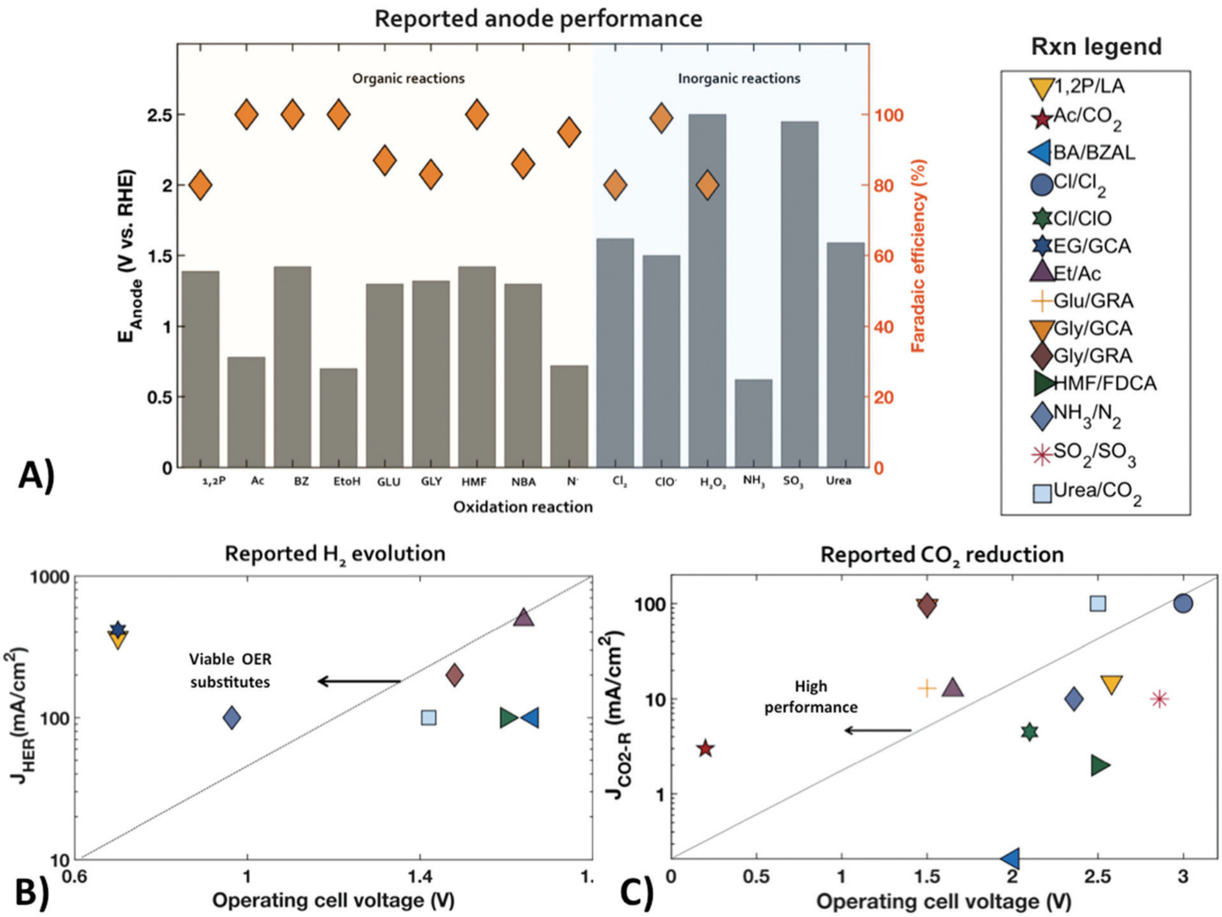

Fig. 2 Performance summary of inorganic and organic OER alternatives for electrolysis. Summary of reported operating potentials (left, bars) at the anode during peak selectivity (right, diamonds) for target reactions [ref. 24, 25, 27 and 47–55] (A) Reported operating cell potentials *vs.* current densities (log-scale) for two-electrode H_2 evolution [ref. 34, 48, 53 and 55–58] (B) and electrochemical CO_2/CO reduction [ref. 14, 24, 49, 51–54 and 59–62] (C) *via* assorted anode oxidations, detailed in the Rxn legend. Reaction acronyms defined in Table S1.†

cing CO_2 at the cathode [ref. 24 and Fig. 2c]. High-rates of CO_2 reduction have also been reported while employing commercial catalysts (*e.g.* RuO_2–IrO_2–TiO_2 DSA plates) to oxidize NaCl to Cl_2 [Fig. 2c]. Such NaCl oxidations have many advantages including mild reaction conditions, cheap raw materials, and a large product demand in fields such as bleaching and industrial waste treatment.[63,64] In addition, highly selective catalysts for these oxidations have been validated at an industrial scale for almost a century, which could greatly accelerate future market penetration.[65] Still, the characteristically high redox potential of these reactions may restrict their deployment to niche markets and moderate-scale operations. Fig. 2c also shows that Cl_2 and ClO^- reactions have some of the highest operating potentials of any OER substitute paired with electrochemical CO_2-R. Highly active catalysts like atomically dispersed Pt–N_4/CNT[66] or Nd-doped IrO_2 [67] could offer ways to reduce costs and operating voltages but are yet to be applied to CO_2 electrolysis. As such, NaCl oxidations may only be reasonable in future electrolysis applications if practical energy efficiencies can be achieved through innovative material and electrolyzer designs.

Like NaCl oxidations, hydrogen peroxide (H_2O_2) produced from water can also demand large energy inputs yet the high market price of H_2O_2 (0.56 \$ kg^{-1})[23] may justify high-energy costs. Fig. 2a shows that peak H_2O_2 FEs of 81% can be achieved at applied potentials of around 2.6 V using zinc oxide (ZnO) nanorods on fluorine-doped tin oxide (FTO).[50] This high performance denotes a large improvement compared to less-efficient catalysts like TiO_2,[68] $BiVO_4$,[69] WO_3,[70] SnO_2 [70] (FEs < 70% at 3 V) and is on-par with other highly-active materials like $CaSnO_3$ (FE = 76%).[71,72] Still, a major challenge of H_2O/H_2O_2 oxidation is the high operating voltages (*i.e.* E° = 1.76 V) that promote competition with the 4-electron OER.[50] Lately, some have deployed photochemical catalysts like $WO_3/BiVO_4$ [73] and TiO_2 [74] to lower overpotentials, though success has been limited.[75] In addition, these designs commonly require added infrastructure that may not be practical at large-scale. As such, more work is needed to improve the selectivity of dark H_2O/H_2O_2 oxidation at lower potentials and clearly demonstrate its feasibility in electrosynthesis applications. Still, the high value of H_2O_2 and use of a convenient feedstock (*i.e.* H_2O) make it an appealing OER substitute worth investigating.

Inorganic oxidations not only can be used to produce value-added chemicals like H_2O_2 but can also treat abundant waste streams that are expensive yet essential to manage. Urea is a major component of human/animal urine and the nutrients (N,P) released during its degradation lead to major environmental problems such as eutrophication and water pollution. Fig. 2c shows that the urea oxidation reaction (UOR) has some of the highest current densities of any reaction coupled with electrochemical CO_2-R. Recently, Ni foam electrodes have been used to pair the UOR with CO_2-R at cell potentials of just 2.5 V under peak cathode efficiencies (FE_{CO} = 90%),[51] outperforming comparable NaCl or SO_3-based oxidations [Fig. 2c]. Similarly, high current densities toward water reduction have also been achieved using Ni–N_3 alloy nanotubes at low cell potentials around 1.42 V (ref. 56) [Fig. 2b]. Other catalysts such as $CeO_2/NiMoO_4$,[76] $MnCo_2O_{4.5}/Ni(OH)_2$,[77] and NiClO[78] have also demonstrated good performance with low onset potentials around 1.3 V. At present, replacing the OER with the state-of-the-art UOR could decrease energy costs by as much as 18% (calcs. in ESI-S2†) and performances are likely to improve. Though promising, a critical drawback of the UOR is that the products are difficult to separate, which may increase capital costs and limit scalability. Still, the UOR's potential to tackle abundant waste streams and generate valuable chemicals (*i.e.* carbonates) make it a promising co-valorization option to consider.

Related to urea, ammonia is another abundant pollutant that is routinely discharged into the environment *via* sources like agricultural wastewater runoff. Notably, the ammonia oxidation reaction (AOR) can be used to manage toxic nitrogenous compounds at very low theoretical potentials (−0.77 V) while supplying cheap electrons for electrolysis at the cathode. In addition, this process can serve as a price-competitive alternative to slow biological ammonia removal processes and can also generate high-value H_2 at the anode ($NH_3 \rightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2$), yielding tremendous economic benefits. The AOR is typically sluggish at room temperature, requiring high overpotentials on transition metals like Pd, Rh, Ru, Au, and Cu,[79] but recent work has noted that metals such as Pt, Ir, and Ni have optimal binding energies for M–N intermediates that can improve AOR reaction rates.[80,81] For instance, a ternary PtIrNi catalyst[79] has recently achieved high current densities around 100 mA cm^{-2} at some of the lowest operating potentials (0.621 V) of any OER alternative [Fig. 2a]. Similar alloys like N-doped NiZnCu layered double hydroxide (LDH) have also been applied towards water electrolysis, achieving high current densities up to 100 mA cm^{-2} (ref. 82) [Fig. 2b]. In addition, some have also used catalysts like Pt/C[51] to couple the AOR to CO_2 electrolysis, albeit at low current cell densities around 10 mA cm^{-2} [Fig. 2c]. Nevertheless, this work is promising and can serve as the foundation for future operations that leverage the AOR to manage abundant toxic waste streams at low energy costs, while also generating high-quality H_2 and green electrons for sustainable electrolysis processes at the cathode.

2.2. Organic oxidations

Organic oxidation reactions (OORs) using alcohols, amines, and various biomass-derived compounds have recently received a lot of attention as potential OER alternatives.[57,83] Fig. 2 includes the applied potentials of 9 OORs at peak selectivity and their performance in coupled electrolysis applications. At large, OORs can be conducted at low potentials, utilize low to zero cost substrates, and generate a wide-range of valuable building-block molecules and products.

Fig. 2a shows that biomass-derived feedstock like ethanol, acetate, glucose, and 1,2-propanediol can be oxidized at anode potentials between 0.7–1.3 V with high selectivity. Notably, the oxidation of ethanol can be conducted at very high FEs around 99% using Ruthenium[55] or Co_3O_4 [84] nanoparticles. Owing to its low standard redox potential (0.06 V), high current densities of 492 mA cm^{-2} have been achieved at applied potentials of 1.64 V, with high H_2 productivity (3000 L m^{-2}) at the cathode[55] [Fig. 2b]. Comparable performance has been demonstrated with ethylene glycol (EG) and 1,2-propanediol oxidations [Fig. 2b]. Similar to ethanol, glucose can also be oxidized at low voltages (1.3 V) with high FEs around 87% [Fig. 2a]. Recently, some of the highest current densities towards H_2 evolution (200 mA cm^{-2}) have been demonstrated using nickel iron oxide (NiFeOx) catalysts[57] for glucose oxidation at the anode [Fig. 2c]. Other catalysts such Fe_2P have also demonstrated good activity for glucose oxidation attaining reasonable current densities (10 mA cm^{-2}) for H_2 at low cell voltages (1.22 V).[85] These results are promising as glucose is a cheap and abundant organic molecule and its product, glucaric acid (GRA), is considered a "top value-added compound" for its uses in biodegradable polymers, biodegradable detergents, and metal complexation agents.[57,86] Altogether, the low-operating potentials and high current densities of these biomass-derived OORs make them prime OER substitutes. For instance, replacing the OER with ethanol oxidation could decrease energy inputs by 43–56% (calcs. in S2†). Still, the majority of present studies have been focused on electrochemical H_2 evolution applications and more work is needed to verify their performance in coupled electrochemical CO_2-R systems. In addition, higher current densities on the order of Amps per cm^2 need to be demonstrated at commercially relevant scales and detailed technoeconomic analyses (TEA) are needed to assess whether the use of high-grade chemicals, as used in these lab scale demonstrations, makes economic sense. Similar evaluations should also be done on even cheaper and more abundant industrial wastewaters that often contain such compounds.

In addition to these reactants, other biomass-derived compounds like 5-hydroxymethyl furfural (HMF) can be oxidized at low anode potentials (1.43 V) [Fig. 2a]. It's product, furandicarboxylic acid (FDCA), is considered a key replacement of terephthalic acid in the generation of polyamides, polyesters, and polyurethanes and holds an exceptionally high market value (\$32–580 kg^{-1}).[83] Several recent electrochemical and photochemical studies have shown excellent conversion efficiencies (*ca.* 100%) of HMF to FDCA at low-potentials using catalysts like NiBx,[87] CoP,[32] or photo-assisted $BiVO_4$.[88] Notably, HMF oxidation can be coupled to H_2 generation with high current densities around 100 mA cm^{-2} using nickel–sulfur (Ni_3S_2) catalysts[34] or CO_2-R to formate using nickel oxide (NiO) nanoparticles,[62] albeit at low current densities (about 2 mA cm^{-2}) [Fig. 2b and c]. The low operating potentials, excellent conversion efficiencies, and high-value of FDCA make HMF oxidation one of the most promising OER substitutes to date. Still, foreseeable roadblocks may exist in large-scale sourcing/processing of HMF and the costs of FDCA separation.[89]

Like inorganic reactions, OORs can also be used to treat waste compounds that are costly to manage. Glycerol is a common waste by-product of biodiesel production that can be used as a near zero-cost substrate to produce glyceric acid (GCA), a building block for polymeric materials,[90] along with other valuable products such as formic acid, lactic acid, gluconic acid, and glyceraldehyde.[14] Lately, materials like organometallic Co-DPPE[91] and AuPt[92] have shown promising current densities (44–50 mA cm^{-2}) for glucose oxidation, and others using STEMPO immobilized on ITO[47] have demonstrated similar current densities with high FEs (83%) at the anode [Fig. 2a]. When paired with electrochemical CO_2 reduction to CO, some of the highest current densities (95 mA cm^{-2}) of any OER substitute have been achieved using Pt/C for glycerol oxidation[14] [Fig. 2c]. In addition, replacement of the OER with glycerol co-electrolysis has been reported to reduce energy demands by up to 53% in CO_2 electrolyzers.[14] This data is encouraging as the combined benefits of treating an industrial waste while generating high-value products at low cost makes glycerol oxidation an attractive OER substitute that can boost profits while reducing the environmental footprint of current biodiesel production.

Aside from these biomolecules, high FEs have also been achieved from alcohol oxidations (*e.g.* benzylic alcohol) using catalyst like nitrogen-doped carbon (NC) on $CuCo_XNx$[93] but the overpotentials of these reactions are still relatively high [Fig. 2a]. Likewise, amine oxidations (*e.g.* *n*-butylamine to *n*-butyronitrile) can also demand high overpotentials even with state-of-the-art catalyst like NiFeOx oxyhydroxides.[25] Still, their role in production of valuable imines, nitriles, amides, and amine oxides[94–96] is appealing so more work should be done to lower operating voltages and test their performance in electrosynthesis applications.

3. Design considerations

3.1. Abiotic *vs.* biotic catalysts

The bulk of OER alternative reactions have been examined using abiotic (non-living) catalysts to initiate electrochemical[51] or photochemical reactions.[50] These include various metal alloys, nanoparticle oxides, and synthetic organometallic compounds that can provide high reaction rates but are often challenged by poor selectivity, low resistance to corrosion, high cost, and inadequate stability.[97–100] To circumvent these issues some have turned to biologically-inspired catalysts[101] such as enzymes and living cells to initiate various oxidations at the anode.[102] Enzymatic catalysts can generally provide numerous benefits including mild operating conditions, high selectivity, and good resistance to co-solvents/corrosion.[103,104] Previously, enzymes such as glucose oxidase (GOx) and alcohol dehydrogenase (ADH) have been employed in biofuel cell anodes,[105] demonstrating moderate efficiencies for the oxidation of glucose (8.3%)[106] and ethanol (64%),[107] respectively. Still, most enzymes contain their active sites buried deep below their surface,[101] which obstructs their electrochemical communication with the electrode and limits overall current densities.[101,103] In addition, most enzymatic operations still rely on complex co-factor regeneration cycles[107,108] that lower efficiencies, increase costs, and generate problematic waste streams. As such, recent studies have explored the use of whole-cell microbes in place of enzymes or abiotic catalysts at the electrode surface. For example, electroactive bacteria (EAB) can initiate many biological redox reactions that can replace the OER or other abiotically catalyzed reactions. This can potentially lower material costs and improve the sustainability of operations. In the simplest application, EAB are employed in microbial electrochemical systems where they oxidize influent electron donors (often waste organics) and reduce anode electrodes using extra-cellular electron transfer (EET) mechanisms[109] as part of their respiration.[110] EET can either be direct *via* surface-bound cytochromes/nanowires[111,112] or indirect *via* excreted mediators/electron shuttles such as flavins.[113–115] EAB oxidation offers several benefits compared to the OER and other abiotic alternatives: (1) rather than H_2O, microbial redox reactions typically involve the oxidation of organic molecules, which can substantially lower operating potentials. For instance, if using acetate as the electron donor, H_2 could be produced at a theoretical cell potential of just 0.16 V, which is about a tenth of the voltage of the OER.[116,117] Similarly, replacing OER with (waste) organic oxidization in the anode could reduce the thermodynamic barrier of CO_2-R to CO from 1.34 V to 0.24 V;[118] (2) microbes can process a wide-variety of abundant waste streams, simultaneously enabling electrosynthesis and large savings on traditional wastewater treatment; (3) microbes are self-replicating, allowing for stable oxidations over long periods without the replacement of expensive or rare catalysts (*e.g.* enzymes, precious metals); and (4) EAB can thrive at ambient temperatures and pressures, have a wide pH tolerance, do not require oxygen, produce low amounts of biomass, and can operate as open-cultures that avoid sterilization costs.

Indeed such advantages have led to the development of microbial electrolysis cells (MECs) that use electrons and protons generated by EAB oxidation to generate H_2 at the cathode.[119] In a typical setup, EAB form a biofilm on anode electrodes where they oxidize waste organics and use EET mechanisms to transfer electrons through an external circuit to the cathode for abiotic water electrolysis. MECs have been operated with a wide assortment of feedstock including glucose, glycerol, acetic acid, cellulose, sewage sludge, and wastewater.[120,121] Typically a small voltage of *ca.* 0.2–0.8 V *vs.* RHE is applied to initiate the flow of electrons,[122] or the external voltage need can be bypassed by using a photocathode[94] or integrated power management circuit.[123,124] Fig. 2a shows acetate oxidation can be conducted at very high selectivity (*ca.* 100%) at low anode potentials (0.78 V). Likewise, high MEC H_2 production rates (50 m^3 H_2 per m^3 reactor per day) and yields (close to 100%) have also been reported and are constantly improving.[125] In addition to H_2 evolution, MEC-type devices have also been used to generate valuable chemicals such as H_2O_2,[126] degrade pollutants like 4-chlorophenol,[127] and recover nutrients such as nitrogen[128] and phosphorus.[129] Moreover, some have coupled EAB oxidation to the synthesis of carbon products such as methane and formic acid from CO_2.[130] Though promising, microbial electrochemical systems rely on whole cell catalysts that face several scalability challenges such as slow mass transfer rates in low-conductivity electrolytes (*e.g.* wastewater) that limit overall current densities. Nevertheless, whole-cell catalysts could provide a variety of benefits that complement abiotic or enzymatic catalysis towards low-cost and sustainable electrolysis.

3.2. Realistic electrolyte considerations

Electrolytes that replace pure water for anode oxidations can include a wide-range of aqueous and organic-based solutions. Practical electrolyte considerations include operating pH, temperature, conductivity, and waste management strategies. In addition, electrolytes should be inexpensive, abundant, non-corrosive to catalysts, highly conductive, and exclude ions that are difficult to separate from target valorization products.

In mature electrolysis operations, it may be impractical and/or costly to substitute the existing OER for an alternative co-valorization reaction. The typical OER uses a high purity water electrolyte, which can be expensive and unsustainable due to high water demands.[15] Rather than transporting treated water to electrolyzers, high-purity water could be produced *via* on-site purification/desalination techniques.[131] Such processes would, however, inflict significant overhead to production associated with added infrastructure, energy usage, and waste management.[132,133] The cost of commercial-scale water treatment processes like desalination are frequently expensive as \$2–6 $kGal^{-1}$.[134,135] To avoid these costs, some have considered using seawater as an OER electrolyte due to its low cost, abundance, conductivity, and suitable pH. Fig. 3 summarizes the performance of various studies that have used seawater OER at the anode to support H_2 production at the cathode. To date, major challenges have included maintaining a stable pH at the anode, mitigating fouling from non-innocent ions, and increasing selectivity for OER over competing chloride oxidations.[45] Lately, reasonable current densities have been attained using catalysts such as FeOx,[136] NiCo,[137] and NiNS[138] for seawater OER [Fig. 3]. Notably, Dresp *et al.* (2018)[139] recently operated a seawater H_2 electrolyzer at high current densities of 200 mA cm^{-2} using a nickel–iron (NiFe) layered double hydroxide anode at 1.6 V [Fig. 3]. Such breakthroughs, present promising options to lower operating costs and improve the sustainability of large-scale OER.

Though encouraging, the added costs of water transmission (\$120–156 $MGal^{-1}$)[140,141] may restrict the use of seawater OER to coastal communities, so equally cheap and abundant inland water sources (*i.e.* surface water, groundwater, or wastewater) should also be considered. For example, the US alone produces around 60.4 km^3 of municipal wastewater per year[142] that could serve as a virtually free electrolyte source. Such wastewaters are often available in high population areas that also emit large amounts of waste CO_2 and have a high demand for products such as H_2 and energy-dense organics. For instance, New York City consumes about 1.5 billion gasoline gallon equivalents of energy per year[143] while also generating 55 Mt CO_2- e[144] and 475 billion gallons[145] of municipal wastewater per year.

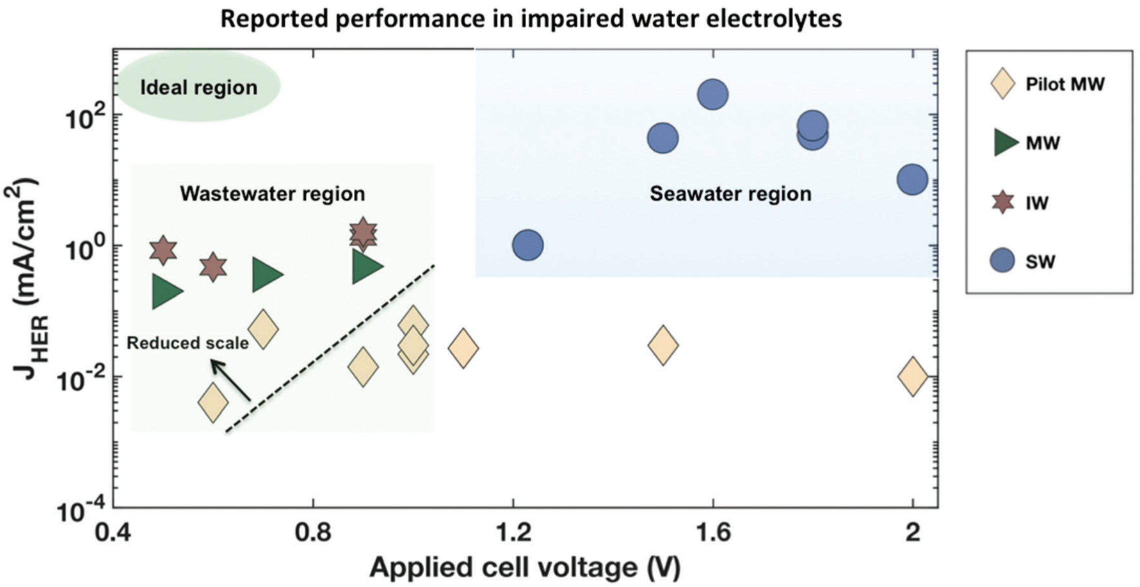

Fig. 3 Comparison of impaired water electrolytes used in H_2 electrolysis. Reported operating cell potentials (*x*-axis) *vs.* current densities (log-scale, *y*-axis) for two-electrode H_2 evolution [ref. 42, 136–139 and 149–158] *via* various impaired water electrolytes. Acronyms: lab-scale seawater OER (SW), MEC using municipal wastewater (MW), MEC using industrial wastewater (IW), and MEC pilot-scale (>1–2 L) using municipal wastewater (pilot MW).

As such, an ideal scenario could be to leverage existing wastewaters in an industrial-scale electrolysis operation that simultaneously accomplishes fuel and chemical synthesis, CO_2 capture and utilization, and wastewater treatment in a single integrated process. Such platforms could not only be used to tackle municipal wastewaters but could also be applied to highly abundant industrial waste streams that are costly to manage. For example, biorefineries typically produce high strength wastewater (80–160 g L^{-1} COD)[146,147] that is rich in organic compounds, which can serve as cheap electron donors for anode oxidations in place of the traditional OER. Effective oxidation of these waste molecules can simultaneously generate clean water while providing low-cost electrons for carbon-negative (or neutral) electrolysis or electrosynthesis of high-value products at the cathode. Indeed, such practices could substantially increase biorefinery profits by (1) generating valuable chemicals, (2) enabling additional carbon tax credits/incentives, and (3) lowering wastewater treatment costs that can routinely account for 30–40% of total plant operating expenses.[148]

Fig. 3 summarizes various H_2 electrolysis studies that have used industrial or municipal wastewater electrolytes at the anode. Though many wastewater oxidations can potentially be initiated *via* abiotic or enzymatic catalysts, the majority of present studies have focused on using whole-cell bacteria to oxidize waste organics in MEC-type reactors [Fig. 3]. Importantly, the oxidation of waste organics has allowed these OORs to take place at much lower operating potentials (0.5–1.2 V) than alternate OERs in seawater or potable water (*ca.* 2.3–2.4 V), highlighting their good potential for energy/cost savings [Fig. 3]. Nevertheless, the current densities (.004–1.6 mA cm^{-2}) of these state-of-the-art reactions have a mean value of 0.36 mA cm^{-2} (variance, 0.22) and are typically been lower than those achieved in seawater or potable water due to slow rates of EET and mass-transfer limitations at the electrode interface[159] [Fig. 3].

Notably, the performance of wastewater oxidations (*via* MEC) seems to be related to the scale of operation and composition of the wastewater electrolyte. For example, reactors using municipal wastewaters (MW) with sizes below 1 L frequently achieved around 16–18 times greater current densities than those at larger scale (>1–2 L, pilot) using similar MW electrolytes [Fig. 3]. This can generally be attributed to high internal resistances caused by ineffective mixing/mass transfer in the pilot-scale systems.[42] Similarly, industrial wastewaters (IW) seem to support higher current densities than MW, as reactors of similar volumes using IW enriched with glucose or glycerol,[153] often achieved 3–4 times higher current densities than those using MW at similar operating potentials [Fig. 3]. This is likely because IW can frequently provide higher conductivities and greater organic loadings that support microbial growth and faster rates of electron transfer.[153]

Though several challenges exist, the combined benefits of lower energy demands, reduced electrolyte costs, generation of valuable products, and treatment of costly waste streams, makes the use wastewater electrolytes one of the most promising co-valorization options available for electrolysis to date. As such, future research is needed to improve the scalability of reactor configurations and develop efficient catalysts that can achieve high current densities in a range of wastewater compositions.

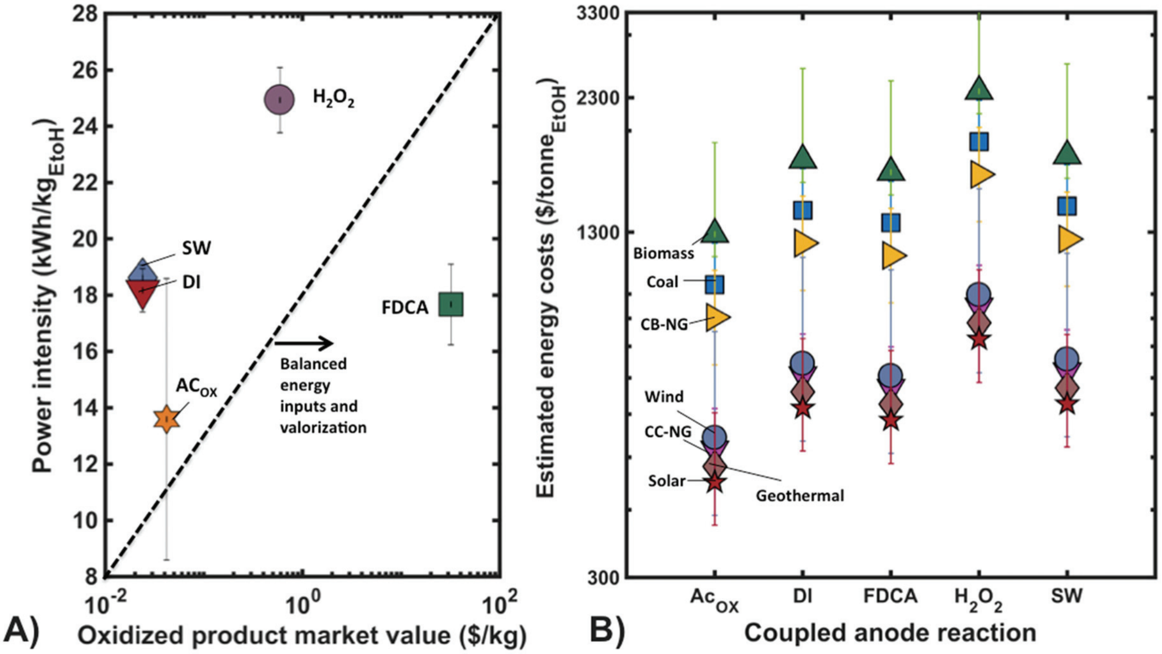

Fig. 4 Power intensities and estimated energy costs of various oxidation scenarios. Current market price of anode products (log scale, *x*-axis) with corresponding power demands for coupled cathodic CO_2-to-ethanol conversion (*y*-axis) *via* assorted anode reactions (markers) (A) energy costs per tonne of ethanol produced in a CO_2 electrolyzer using various anode reactions (markers legend) and power sources. (B) Costs based on an average of levelized costs of energy (LCOE) with range shown in error bars; select power acronyms: combustion cycle natural gas (CB-NG), combined cycle natural gas (CC-NG). Anode oxidations defined as standard OER (DI), OER using seawater electrolyte (SW), acetate oxidation (AC_{OX}), H_2O_2 generation *via* H_2O oxidation (H_2O_2), FDCA production *via* HMF oxidation (FDCA).

3.3. Expected energy input and costs

Energy costs are a major barrier to large-scale electrolysis and are highly dependent on source, location, availability, and existing governmental policies/incentives.[160] Fig. 4 summarizes exemplary energy inputs and costs of cathodic CO_2-to-ethanol electrosynthesis using various reactions at the anode [calcs. provided in ESI S3†]. These oxidations were chosen due to their low-energy inputs and/or the high market value of their products to assess the economic viability of OER substitutes. A brief comparison of the following results to conventional bioethanol fermentation is provided in the ESI [S4].† Average power intensities range from 13.6 to 24.9 kW h kg^{-1}, depending on the applied potential of the oxidation reactions, with the lowest energy inputs required for OORs like acetate oxidation (13.6 kW h kg^{-1}) and HMF/FDCA oxidation (17.7 kW h kg^{-1}) [Fig. 4a]. Notably, the energy demands of the HMF/FDCA oxidation are amongst the lowest while the market price of FDCA ($32 per kg) is orders of magnitude larger than the products from alternative reactions. Average power intensities for each oxidation scenario were used to approximate costs of electrosynthesis using levelized costs of energy (LCOE) from a recent U.S. Energy Information Administration (EIA) report[161] [Fig. 3b]. As expected, costs were highly dependent on the energy source used. For instance, if using seawater OER with a fossil fuel like coal, production costs can be as high as $US 1233–1730 per tonne compared to just $US 522–843 per tonne when using renewable energy from solar photovoltaics (PV) [Fig. 4b]. This price gap is prompted by current tax incentives and is likely to be highly variable upon location. However, the retail price of renewable power is projected to steadily decrease due to improved technologies, economies of scale, and strengthened supply chains.[162] Importantly, substituting the OER for an OOR like acetate oxidation can still lead to substantial savings of around $140–220 per tonne even when using the same cheap power source like solar PV [Fig. 4b]. These costs estimates are in-line with comparable economic analysis[7] and highlight the importance of electricity costs for scalable electrolysis.

4. An example comparison of OER alternatives for large-scale electrolysis in Los Angeles, CA

The United States is a major GHG contributor with annual emissions of over 20 tonnes-CO_2 equivalents per capita.[163] California (CA) is the nation's most populous state and is the second largest total energy consumer behind Texas.[164] Almost half of CA's electricity is supplied by renewable sources and is expected to increase to 100% renewable (retail) electricity by 2045.[165] In-line with these initiatives, CA's renewable energy infrastructure and lack of freshwater supply present a promising environment for early adoption of large-scale electrolysis using OER alternatives in the anode. Such low-carbon technologies can also benefit from the state's GHG reduction policies/incentives that accompany the CA Global Warming Solutions Act of 2006.[166]

Los Angeles (LA), as the largest city in CA, consumes around 26 million MWh of electricity per year.[167] Fig. 5 shows the estimated electrolysis costs and profits if LA were to replace 20% of their yearly energy demand with H_2 produced *via* various coupled anode reactions (calcs. provided in ESI S5†). A total of five oxidation scenarios were considered with an emphasis on varying key operating parameters such as electrolyte source, cell voltage, and market value of the products. Again, these alternate oxidations were chosen due to their low-energy inputs and/or the high market value of their products.

The significance of electrolyte costs was initially probed by comparing the traditional freshwater OER (DI-OER) with seawater OER. Based on previous reports, this can be done at operating voltages of around 1.73 V if performance with catalysts like NiFe double hydroxide can be adequately scaled[139] [Fig. 5a]. The combined impacts of decreasing both the electrolyte costs and operating voltages were then evaluated *via* an MEC type operation that replaces freshwater anolyte with inexpensive wastewater and substitutes water oxidation with the oxidation of waste organics (*i.e.* acetate to CO_2). Here it is envisioned that whole-cell biocatalysts on the anode can consume waste organics/nutrients from municipal wastewaters, providing electrons and protons for H_2 production at the cathode and partially treated water for subsequent advanced water treatment processes. It is anticipated such systems can be operated at moderate potentials around 0.83 V as commonly reported in MEC pilot-scale studies[42,158] [Fig. 5a]. As such oxidations can often produce low-value end products, the impact of greatly increasing the market value of anode products was explored by considering OER alternatives like the inorganic oxidation of H_2O to H_2O_2 and organic oxidation of HMF to FDCA (eqs. listed in S5†). As previously described, these reactions can generate higher value anode products and be operated at modest cell potentials of 2.25 V for H_2O_2 production[50,70] and 1.47 V (ref. 34 and 168) for FDCA synthesis, respectively [Fig. 5a and Table S2†]. For all oxidation scenarios, the respective amounts of anode products were

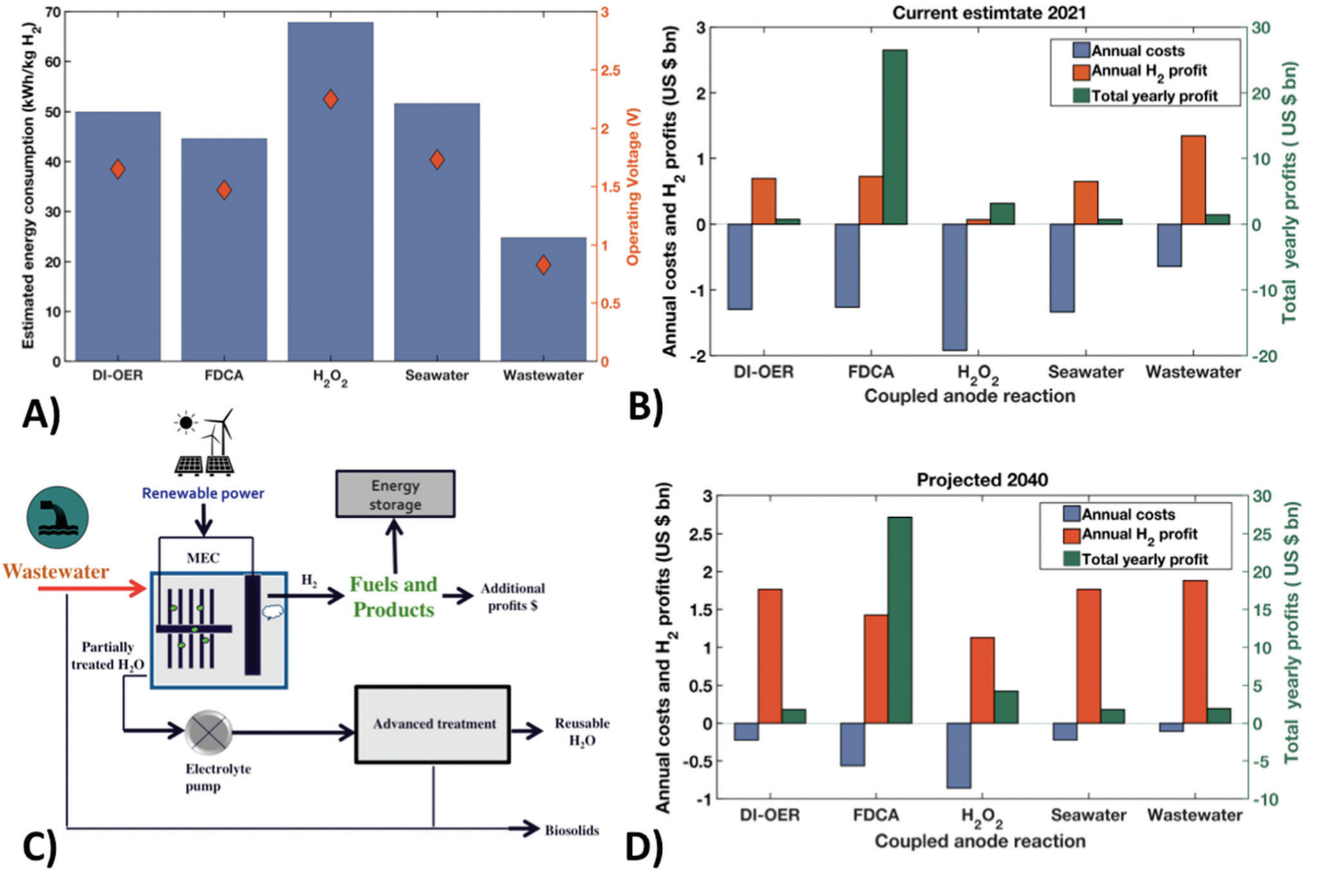

Fig. 5 Comparison of H_2 electrolysis costs and profits using various co-valorization tactics in LA, California. Estimated energy demand of electrochemical H_2 production (*y*-axis, left) and operating voltages (*y*-axis, right) *via* assorted anode reactions (*x*-axis) (A); plant schematic of microbial electrolysis (MEC) for concurrent anodic wastewater treatment and H_2 production (C); projected water electrolysis costs and profits from H_2 sales alone (left, *y*-axis) and combined H_2 and anode products sales (right, *y*-axis) in Los Angeles, California in 2021 (B) and 2040 (D); anode oxidations defined as standard OER (DI-OER), OER using seawater electrolyte (seawater), waste organic oxidation (wastewater), H_2O_2 generation *via* H_2O oxidation (H_2O_2), FDCA production *via* HMF oxidation (FDCA).

directly calculated using mass-balance equations set to satisfy 20% of LA's annual energy demand with 154 ktonnes H_2 generated at the cathode [Table S4, ESI S5†].

Since LA is located on the coast, seawater OER could be a convenient option to replace the traditional OER in large-scale electrolysis. Substituting traditional DI-OER with seawater OER could potentially lower operating costs (from H_2O use) by around $2.5 million per year while avoiding about 370 MGal of freshwater use annually [Table S4† and Fig. 5b]. Still, energy demands for seawater OER would be about 2 kW h kg^{-1} H_2 greater than DI-OER due to the increased operating voltages needed to avoid electrode fouling and competing redox reactions [Fig. 5a]. As such, yearly electrolysis profits (*ca.* $700 million year) would be similar using either freshwater or seawater electrolytes at the anode due to increased energy expenses [Fig. 5b]. In contrast, the use of wastewater electrolytes could lead to substantial savings by reducing operating voltages while also circumventing freshwater needs. For example, the oxidation of waste organics rather than H_2O (*via* DI-OER) could decrease operating voltages from 2.3 V to 0.83 V, leading to around a 93% increase in net profits [Fig. 5a and b]. This is a feasible large-scale approach as an operation of this scale would require about 1 MGal of wastewater per day and LA currently produces around 580 [169] times that amount, presenting a nearly inexhaustibly source of low-cost electrons and water. Still, present H_2 production rates (*via* MEC) will need to improve to realize such benefits at scale.[170]

Nevertheless, maximizing total yearly profits requires increasing the market value of products at the anode as both the oxidation of waste organics to CO_2 ($.04 per kg) and the OER (creating O_2, $.02 per kg) generate relatively low-value commodities. Fig. 5b shows that the combined profits from anode and cathode products can far exceed those from just cathode products (*i.e.* H_2 sales) alone. For example, additional profits of $2.4 bn per year could be achieved if H_2O_2 (2.6 MT) produced alongside H_2 can be sold at a retail price of $0.59 per kg (ref. 23) [Fig. 5b and Table S4†]. Similarly, organic oxidation of HMF to FDCA could also generate sizable profits of around $26 bn per year, owing to low operating potentials and the exceptionally high-market value of FDCA [Fig. 4a]. Notably, the profits of these operations may even increase when considering future market factors.

Fig. 5d shows the adjusted cost and profit estimates for year 2040 based on energy cost predictions from a recent EIA report.[161] Future energy prices are predicted to decrease considerably, increasing profits across all oxidation scenarios [Fig. 5d]. Anodic H_2O_2 or FDCA generation would remain the most economic strategies, however, the relatively high water and energy uses (*e.g.* 44–67 kW h kg^{-1} H_2) of these methods could potentially lead to substantial drawbacks related to large water footprints and hefty CO_2 emissions. As such, the theoretically low energy and potable water uses of wastewater oxidation make it a promising option in terms of both sustainability and future profits. For example, electrolysis operations that replace the traditional anode OER with wastewater oxidation could save about 25 kW h kg^{-1} H_2 and generate an additional $128 million dollars of profits per year [Fig. 5a and d]. Additional benefits can also be obtained by wastewater treatment savings and water-reuse (not quantified). Such integrated wastewater systems are in-line with trends toward decentralized urban water treatment currently under development.[171]

Though promising, large-scale operations such as these will need to carefully consider environment health and safety aspects of their niche application. In general, these can include detailed accounting of GHG emissions (indirect and direct), waste management techniques, and environmental impact assessments. For instance, seawater electrolysis could potentially influence the surrounding ocean ecology or by-products of H_2O_2 (or HMF/FDCA) separation may be hazardous wastes that require unique disposal methods. Such concerns should be meticulously addressed in future life-cycle assessments as these technologies are scaled-up. In addition, large-scale electrolysis operations should ensure plant safety by avoiding the formation of dangerous chemical mixtures that can form *in situ*, as those routinely found in modern H_2 electrolyzers that use the traditional OER (*i.e.* explosive H_2/O_2 mixes[16]). For instance, reactive molecules such as H_2O_2 or Cl_2/ClO^- could potentially combine with H_2 or CO_2-R products, generating flammable mixtures. As such, future electrolyzer designs should consider implementing devices like ion-exchange membranes,[172] ion-permeable separators (*e.g.* metal–oxide diaphragms[173]), or thin product extraction chambers[174] that mitigate product cross-over. Such designs have been effectively employed in industrial-scale electrochemical systems like the chloro-alkali processes[175] and can be applied to related electrolysis operations towards improved safety and maximized profits.

5. Technical steps towards scalable anode co-valorization

Many alternative anode reactions present promising opportunities to replace the conventional OER while potentially generating substantial add-on economic and societal benefits. Still, future research efforts should aim to improve the scalability of state-of-the-art processes by addressing key limitations in material costs, kinetics, and long-term reactor stability.

Notably, several OER alternatives use expensive catalysts (*e.g.* precious metals) that can drag the value proposition of electrolysis operations [Tables S5–S7†]. For instance, if operating with 1 kg of catalyst, replacing an precious metal such as Pt ($998 per ozt)[176] with a cheaper transition metal like nickel ($.54 per ozt)[176] can reduce costs around $32 000, leading to significant savings at large-scale. As such, it is crucial that researchers develop sustainable, low cost, and efficient catalysts that can support fast production rates and long-term reactor stability.

In general, the kinetics of abiotic catalysts can be improved by tuning material properties such as particle size,[177] surface roughness,[178] crystal facet expression,[179] and surface binding energy.[180] Recent studies showed using free energy diagrams to predict (1010) and (0001) facets on ZnO were an effective method to select active and stable catalysts for H_2O_2 production.[50] Likewise, modulating the oxidation state of Ni active sites was used to tune *COO binding energies and promote more rapid UOR kinetics.[78]

To complement new materials, future studies can further improve kinetics by accelerating mass-transfer at the electrode surface *via* rapid-mixing, advanced flow-fields designs,[181] and/or increasing the operating temperatures/pressures. A recent thermo-electrochemical hybrid process using a solid acid electrochemical cell (SAEC) achieved exceptionally high current densities for ammonia oxidation and impressive efficiencies for H_2 production (*ca.* 100%) while operating at 250 °C.[182]

At large, similar tactics that involve improved material and reactor designs can also be applied to biotic catalysts. Recent calculations have suggested that promoting EAB biofilm growth with new 3D electrode materials can boost current densities up to 1 A cm^{-2} in MEC-type reactors[159] and combining these materials with state-of-the-art gas diffusion electrodes,[183] bubble-columns,[184] or hollow-fiber membranes[185] can likely further improve kinetics.

In addition, breakthroughs in genetic engineering[186] (*e.g.* CRISPR) or adaptive lab enrichment[187] can be leveraged to further boost microbial metabolisms and cell tolerance of high temperatures (*i.e.* thermophiles)[188] high salinities (*i.e.* halophiles)[189] or extreme pH[190] that may also promote fast redox rates. For example, EAB such as *Acidiphilium cryptum* can tolerate very low operating pH (2.5)[190] after several adaptive enrichment cycles, making them more amenable to conditions that promote H_2 synthesis.

Nevertheless, intense reactor conditions that accompany high current densities may also be detrimental to the overall reactor stability, especially when using sensitive abiotic catalysts. For instance, pH near the electrode surface has shown to change 5–9 pH units (*vs.* the bulk) during seawater electrolysis,[191] leading to increased overpotentials and catalyst deactivation.[192] As such, further development of tools such as protective catalyst films[193] and decoupled reactor configurations[194] are needed to help mitigate such effects. Some have recently used solid-state redox materials to isolate H_2O_2 production at the anode,[195] demonstrating a step in this direction. Similar devices could also enable abiotic catalysts to more effectively operate in impaired water electrolytes like wastewater where fouling *via* microbes, obstructive particulate matter, and non-innocent ions may be severe. Though biocatalysts can achieve excellent stability (3–12 months) in a variety of wastewaters,[151,196,197] progress towards new electrode materials,[198] reactor designs, and protective cell coatings[199] may be useful to extend stable operation periods at higher current densities and larger reactor scales.

6. Outlook

The quantitative review and calculations provided in this study show numerous alternatives to the conventional OER in electrolysis that can yield significant economic and societal benefits. Still, many of these pathways are nascent and need to overcome various challenges to improve scalability and performance. In general, each of the scenarios may be suited to niche applications as it may be difficult for a single solution to meet and balance multiple objectives that can include maximized profits, low water-footprint, limited GHG emissions, and long-term stability/feasibility. Alternative OER reactions involving both inorganic and organic molecules present many worthwhile options that can generate substantial add-on profits. Industries can leverage these processes to produce feedstock chemicals required for other processes that are housed at the same facility and take advantage of existing purification, distribution, and waste-management infrastructure. For instance, ethanol biorefineries generate high strength wastewater and high purity waste CO_2, which can be an ideal combination for concurrent wastewater treatment and CO_2 electrolysis-to-ethanol. In general, OER alternatives can use mature operations like the chloro-alkali process as useful models towards market transformation. In particular, a reaction like HMF/FDCA oxidation is an attractive OER alternative due to its low-operating potentials, high conversion efficiencies, and high market value of target products. Still, OORs like this have almost exclusively been demonstrated at the lab-scale, and data coupling this oxidation with parallel cathodic H_2 evolution or electrochemical CO_2-R has been scarce. As discussed, the kinetics of this reaction (and other OER alternatives) should also be improved, as relatively high-energy inputs are required for peak selectivities. Universally, future research initiatives need to advance reactor configurations and optimize materials for alternative inorganic or organic reactions to become practical at the commercial scale. Considerations must be made for reactant supply/availability and the market size of end products. In addition, the environmental impact of individual processes should be assessed to determine how their GHG emissions, water demand, and waste generation compare to the conventional OER and other options.

At large, the sustainability of the OER and alternate oxidations can be improved by replacing high-quality water electrolytes with impaired water sources (*e.g.* seawater or wastewater). Such practices can decrease operational costs and greatly reduce water footprints of electrolysis. This is important as a third of the worldwide population lacks clean water and could face trade-offs between drinking water and energy supply.[200] Recently, processes like seawater OER have made significant progress and several studies have achieved modest current densities (43–67 mA cm^{-2}) using real seawater electrolytes.[137,155] Still, many technical obstacles including electrode corrosion, pH control,[191] fouling, competing redox reactions,[192] and low-energy efficiencies, must be overcome for seawater OER to be feasible at large-scale. Lately, designs involving permiselective catalyst coatings[193] and optimized OER surface binding sites,[201] show good potential to improve overall performance metrics. Such innovations could also be applied to impaired in-land water sources (*e.g.* wastewater, surface waters, or ground waters) that will likely face similar challenges related to obstructive particulate matter, microbial fouling, and the existence of non-innocent ions. Complementary to seawater sources, wastewater treatment facilities are often located in population centers and near industrial CO_2 point sources (such as power plant, refineries, cement plants, *etc.*)[20] that are routinely challenged by energy storage, CO_2 emissions, and water use issues.[202,203] A single-integrated electrolysis process could solve multiple challenges by cleaning up wastewater at the anode, generating reusable water for on-site processes, and capturing/upgrading CO_2 into value-added fuels and chemicals. Researchers are currently working to translate such technologies to the market, and are addressing various performance issues by adapting microbes to hyper saline media to support higher current densities,[204] developing new catalysts that effectively operate at neutral pH,[205] and constructing novel reactors that physically decouple anode and cathode reactions.[206,207]

As research continues to advance, an assortment of anode co-valorization techniques will likely become available to future electrolysis operations. Still, many approaches will only be suitable in fit-for-purpose designs and commercial adoption will highly depend on the available water source, electron donors, energy costs, and product demands. As such, careful techno-economic analyses (TEA) and additional CAPEX/OPEX reports would be useful to help identify niche markets where anode and cathode reaction products could be efficiently coupled. In addition, more life-cycle assessment (LCA) studies are needed to evaluate the environmental impacts of the various OER alternatives to ensure they support important global initiatives like the UN SDG 6 on Clean water and sanitation and UN SDG 13 on Climate Action.[208] Nevertheless, advancements towards effective anode co-valorization can indeed maximize future profits, accelerate market penetration, and greatly improve the sustainability of commercial electrosynthesis.

Conflicts of interest

There are no conflicts to declare.

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