Available online at www.sciencedirect.com

ScienceDirect

Current Opinion in Electrochemistry

Review Article

Comparative assessment of alkaline and acidic electrochemical reforming of bio-ethanol for hydrogen and value-added chemicals production

Ilaria Perissi, Marco Bellini, Enrico Berretti, Maria Vincenza Pagliaro and Alessandro Lavacchi

Electrochemical reforming (ER) of biomass-derived oxygenates offers an industrially viable route to coproduce high-added-value chemicals and green hydrogen at lower voltages than conventional water electrolysis. Over the past five years, more than 200 studies have demonstrated rapid advances, with both proton exchange membrane (PEM) and anion exchange membrane (AEM) systems achieving industrially relevant current densities (1 A cm^{-2}) at cell voltages even below 1 V. For these systems, the electrolyte pH has a profound influence on the process through reaction pathways, catalyst and membrane stability, and even on overall reaction stoichiometry. In this opinion, we provide a critical comparison of the often-overlooked differences between acidic and alkaline technologies, highlighting their distinct thermodynamic, kinetic, mass-balance and energetic trade-offs, to define the research priorities in the path towards the scale-up and deployment of high-added-value chemicals.

Addresses
National Research Council of Italy, Institute of Chemistry of Organometallic Compounds (CNR-ICCOM), Via Madonna del Piano 10, 50019, Sesto Fiorentino, Italy

Corresponding author: Lavacchi, Alessandro (alessandro.lavacchi@cnr.it)

Current Opinion in Electrochemistry 2026, **60**:101936

This review comes from a themed issue on **Electrochemical Materials and Engineering (2026)**

Edited by **Neil V. Rees**

For a complete overview see the Issue and the Editorial

Available online 3 September 2026

https://doi.org/10.1016/j.coelec.2026.101936

2451-9103/© 2026 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

Introduction

Electrochemical reforming (ER) is a water-like electrolysis technology that replaces the oxygen evolution reaction (OER) with the multielectron oxidation of organic substrates. Organic substrate oxidation is thermodynamically more favourable than water oxidation [1] allowing for lowering the ER cell potential while coupling green hydrogen production with the synthesis of sustainable value-added chemicals [2].

Among the potential feedstocks, bioethanol is particularly attractive due to its renewable origin, high hydrogen content and low toxicity; hence, it is usually considered as a reference organic substrate (as in the present article) to provide a scalable framework for more complex bioalcohols. Its practical relevance has also been demonstrated using real waste-derived and fermented bioethanol streams, confirming the feasibility of ER under realistic feedstock conditions [3]. More complex biomass-derived substrates, such as glucose [4] and lignin [5,6], have also recently emerged as promising candidates, broadening ER from small-molecule alcohol oxidation towards carbohydrate upgrading and selective bond-cleavage chemistry.

Other biomass-derived reactants, such as glycerol [7], a major byproduct of biodiesel production, and 1,2-propanediol, represent interesting substrates for ER [8–11]. These polyols enable the selective oxidation towards high-added-value C_2–C_3 products, including acetate, lactate and formate [12] (and their relative salts under alkaline conditions), which are key intermediates for polymer, solvent and chemical manufacturing [13–16]. ER of these bioalcohols has been extensively investigated in both acidic and alkaline environments, showing their excellent potential as precursors for an energy-efficient and waste-enabled biorefinery key process [17,18].

As in water electrolysis and direct alcohol fuel cells, ER can be implemented in membrane reactors that may exploit either a proton exchange membrane (PEM) or an anion exchange membrane (AEM) [19,20]. The membrane's characteristics define the device's operating pH, which can be either acidic or alkaline. The pH of the ER governs reaction thermodynamics, kinetics, product formation (carboxylates vs. free acids), materials' stability, stoichiometry and system-level mass and energy balances.

However, despite extensive literature on catalyst development and reaction mechanisms, the broader system-level implications of acidic versus alkaline ER remain comparatively underexplored, particularly regarding reagent consumption, product separation and overall energy efficiency. In particular, alkaline configurations may require significant alkali management and regeneration, an aspect often overlooked in favour of voltage efficiency, selectivity and process intensity [21].

In this opinion, we provide a critical comparison of acidic and alkaline ER beyond catalyst-level performance, focusing on the interplay between thermodynamics, stoichiometry, mass balance, energetics and techno-economic constraints. This system-level perspective represents the main contribution of the present work and aims to identify the most viable pathway for scalable hydrogen and value-added chemical production.

Thermodynamics and kinetics

Ethanol electrooxidation can proceed via multiple pathways: e.g. partial oxidation to acetaldehyde ($2e^-$), oxidation to acetic acid/acetate ($4e^-$) or complete oxidation to carbon dioxide (CO_2)/carbonate ($12e^-$). The selectivity depends on catalyst composition, applied potential, electrolyte pH and operating temperature. *In situ* [22] and density functional theory (DFT) studies [23] show that acidic media favour partial oxidation by stabilising C_2 intermediates, whereas alkaline media promote C–C cleavage and deeper oxidation.

Table 1 reports the 4-electron pathway, the dominant route under practical conditions, and adopts it here as the reference case for comparing mass balance and energy requirements [21].

The overall reaction is thermodynamically spontaneous in alkaline conditions but slightly unfavourable in acidic media, requiring applied bias with reported onset potentials around 0.35–0.4 V versus reversible hydrogen electrode (RHE) [24–26], above the thermodynamic potential predicted from ΔG° in both cases. The enthalpy change differs significantly: +78.3 kJ/mol in acidic versus +24.2 kJ/mol in alkaline systems, indicating that the reaction is more endothermic in acid and less in alkali [27].

Reaction mechanisms also differ markedly. In acidic media, ethanol oxidation on platinum (Pt)-based electrodes proceeds via dissociative adsorption, forming acetaldehyde (HCHO) below ~0.6 V versus RHE, while higher potentials promote hydroxide (OH)-assisted pathways leading to acetic acid, which typically dominates at around 0.9–1.0 V [28,29]. Electrode materials can favour parallel reaction routes, lowering operational potentials and improving oxidation efficiency, as observed by Pt alloyed with oxophilic metals, such as tin (Sn), nickel (Ni) or rhodium (Rh) [30,31]. In alkaline media, bioalcohol oxidation proceeds through OH-assisted dehydrogenation with faster kinetics, although local hydroxyl ion (OH^-) depletion and high bulk alkalinity can limit performance and accelerate degradation [21,32–34].

These differences directly affect catalyst and device selection, but their broader impact emerges at the process scale, where mass balance and energy consumption become decisive.

Materials and device architectures' overview

For optimal performance, both alkaline and acidic ER systems rely on platinum-group metal (PGM) catalysts. Alkaline ER enables rhodium-based and palladium-based catalysts that achieve mass activities exceeding 2470 mA mg_{Rh}^{-1} [35] and 1176 mA mg_{Pd}^{-1} [36] and advanced nanostructuring strategies, like core-shell architectures (Ru@Pt) [37], mesoporous frameworks (RhPt-mesoporous structures [MPS]) [38] and trimetallic nanowires ($Pt_6Ni_2Rh_3$) [39], have pushed mass activities above 2000 mA mg^{-1}. Acidic catalysts mainly rely on Pt–Ru formulations, to withstand low-pH oxidative conditions and rarely exceed 1200 mA mg^{-1} [40,41].

Non-PGM catalysts are available only in alkaline media, albeit with a substantially lower performance [42,43]; as well as in acidic environment, high performances at high pHs are guaranteed as well only using PGM catalysts, especially at the anodic side [35,36].

On the side of the membranes, acidic PEM systems rely on perfluorosulfonic acid membranes (Nafion and analogues) that provide high proton conductivity (0.08–0.12 S cm^{-1} at 80 °C under hydrated conditions) and exceptional chemical stability under oxidative conditions [44]. However, these membranes introduce four critical challenges: (i) high cost ($500–800/$m^2$), (ii) sensitivity to organic crossover that reduces faradic efficiency and (iii) potential chemical participation in side-reactions. In this respect, Nafion acts as a solid acid catalyst [45] promoting acetaldehyde acetalisation to 1,1-diethoxyethane. Furthermore, sulfate anion adsorption from acidic electrolytes poisons catalyst active sites and alters product selectivity, creating complex membrane–electrolyte–catalyst interactions that reduce overall performance [46]; (iv) fluoropolymers like Nafion (per- and polyfluoroalkyl substances [PFAS]) are raising health concerns, and their

Table 1

Thermodynamic comparison of EtOH ER reactions in acidic vs alkaline media (data are from NIST–Chemistry WebBook, SRD 69).

EtOH ER	Acidic media	Alkaline media
Anode	$CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 4H^+ + 4e^-$	$CH_3CH_2OH + 5OH^- \rightarrow CH_3COO^- + 4H_2O + 4e^-$
Cathode	$4H^+ + 4e^- \rightarrow 2H_2$	$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$
Overall reaction	$CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 2H_2$	$CH_3CH_2OH + OH^- \rightarrow CH_3COO^- + 2H_2$
Compounds	**Gibbs Free Energy** (ΔG°f @ 298.15 K, kJ/mol)	
Ethanol (CH_3CH_2OH, l)	−174.8	−174.8
Hydroxide ion (OH^-, aq)	–	−157.3
Water (H_2O, l)	−237.1	–
Acetic acid/Acetate	−389.9 (CH_3COOH, l)	−369.4 (CH_3COO^-, aq)
Hydrogen gas (H_2, g)	0	0
ΔG° reaction	+22	−37.3
	Standard Potential (E° = −ΔG°/nF, V)	
E°cell	−0.057	+0.097
	Standard Enthalpy (ΔH°f, kJ/mol)	
Ethanol (CH_3CH_2OH, l)	−277.0	−277.7
Hydroxide ion (OH^-, aq)	–	−230
Acetic acid/Acetate	−484.5 (CH_3COOH, l)	−483.5 (CH_3COO^-, aq)
Water (H_2O, l)	−285.8	–
Hydrogen gas (H_2, g)	0	0
ΔH_rev	+78.3	+24.2 kJ/mol

EtOH ER, ethanol electrochemical reforming; NIST, national institute of standards and technology; SRD, standard reference database.

employment might be subject to a ban in the near future [47,48].

Alkaline AEM systems offer an apparent advantage due to their lower cost ($200–400/$m^2$), but suffer from severe durability limitations: hydroxide-conducting ionomers degrade via Hofmann elimination and nucleophilic attack. In a recent study, a conductivity drop of 30–50% after 500 h under ER conditions has been observed [49] due to carbonate formation from oxidation reactions that precipitate and block ion transport, increasing cell resistance. Similarly, catalyst deactivation remains a critical challenge in both acidic and alkaline ER systems, mainly due to poisoning by adsorbed intermediates, surface oxidation and structural degradation [50,51]. Regeneration strategies based on potential cycling, cathodic cleaning or periodic polarity inversion have demonstrated partial recovery of catalytic activity, highlighting the importance of integrating durability and recoverability into practical system assessment [52,53].

Recently, membraneless alkaline designs have been proposed, avoiding these issues but requiring continuous electrolyte replenishment and sophisticated product separation, reintroducing operational complexit [54].

Overall, from a material's and device perspective, both acidic and alkaline ER architectures exhibit closely balanced trade-offs rather than a clear intrinsic advantage. Therefore, our discussion moves at the process scale, where stoichiometry and resource flows stem from decisive distinctions.

Mass balance

The choice of acidic or alkaline device architecture directly defines the stoichiometric flows of reactants, electrolyte species and products within the system. In particular, the formation of carboxylate salts in alkaline environments and free acids in acidic media introduces fundamentally different material balances.

Stoichiometric calculations are used to estimate reagent consumption and hydrogen yield per kilogram of dihydrogen (H_2) produced. The analysis highlights the differences in water and sodium hydroxide (NaOH) requirements, as well as the nature of coproducts, acetate in alkaline ER and acetic acid in acidic ER, which have distinct implications for process efficiency, resource management and economic viability.

Considering both alkaline and acidic reactions (Table 1) at 2 mol (4 g) of H_2 per mole (46 g) of ethanol, 1 kg of H_2 requires 11.5 kg of ethanol under both alkaline and acidic conditions. The key difference lies in reagent consumption: alkaline ER requires 10 kg of NaOH, while acidic ER consumes 4.5 kg of H_2O (Table 2).

The hydrogen yield remains identical across alkaline and acidic conditions at 1 kg of H_2 per 11.5 kg of ethanol, confirming that ethanol consumption is not affected by the reaction environment. The alkaline ER process relies

Table 2

Reagents and products' mass balance for ER of EtOH in alkaline and acidic media.

Component	Alkaline ER	Acidic ER
Ethanol Required	11.5 kg	11.5 kg
Water Required (only net stoichiometric water consumption)	0 kg	4.50 kg
NaOH Required	9.98 kg	0 kg
Coproduct	Acetate (CH_3COO^-)	Acetic acid (CH_3COOH)

ER, electrochemical reforming, EtOH, ethanol; NaOH, sodium hydroxide.

on NaOH, whereas the acidic ER process requires an additional 4.5 kg of water per kilogram of H_2 produced. The absence of NaOH in the acidic route simplifies reagent management but increases water demand.

The nature of the coproduct differs significantly; acetate (CH_3COO^-) in alkaline ER may require further separation and neutralisation steps, whereas acetic acid (CH_3COOH) in acidic ER could have potential commercial value, influencing process economics.

Energetics

While the mass balance highlights differences in reagent consumption and product speciation, a complete comparison between acidic and alkaline ER architectures must also consider their energetic implications.

Table 3 reports an extract of literature and estimations by the authors (through Faraday's laws of electrolysis) of energetics related to ER acidic and alkaline systems. This assessment doesn't pretend to be an exhaustive summary, as it is mainly based on pure stoichiometric assumptions, rather it highlights the need to include alkali energy production in the overall assessment of ER for high-added-value chemicals production in alkaline media.

A kilogram of H_2 contains approximately 496.03 mol. In both alkaline and acidic ER, hydrogen evolution involves the transfer of two electrons per mole of H_2. Assuming a voltage of 1 V, the energy required for ER is calculated as 95.72 MJ, equivalent to at least 26.6 kWh/kg of H_2. Indeed, under the considered conditions, acidic systems show energy consumptions ranging from 25.6 [55], [56]to ~37.2 kWh kg^{-1} H_2 [57], while alkaline approaches reach values around ~26.6 kWh kg^{-1} H_2 [21,54].

Moreover, literature suggests a typical operational range of approximately 26–37 kWh kg^{-1} H_2 for the 4-electron pathway. Temperature increase (50–100 °C) affects primarily the kinetics of the reactions, enhancing charge transfer and reducing ohmic resistance. Alkaline systems appear operationally advantageous, as they can sustain higher current densities at lower cell voltages, with overpotentials decreasing to ~0.6–0.7 V at ~60 °C, whereas acidic systems typically require ~1 V or higher even at elevated temperatures [55].

However, when the stoichiometrically consumed alkali is neither recovered within the process nor available as a residual stream from an adjacent industrial operation, alkaline ER is associated with an additional energy penalty related to the external supply of NaOH or potassium hydroxide (KOH). Industrial chlor-alkali membrane cells typically consume approximately 2.1–2.5 kWh per kilogram of NaOH, while alternative production or recovery routes, including bipolar-membrane electrodialysis, may require up to approximately 3.6 kWh per kilogram of NaOH [60]. Considering the stoichiometric requirement of around 10 kg of NaOH per kilogram of H_2 in alkaline ethanol electroreforming, the energy penalty associated with external alkali supply may amount to approximately 21–36 kWh per kilogram of H_2. Under this assumption, the electrochemical energy demand of approximately 26.6 kWh kg^{-1} H_2 at 1 V would result in a total system-level energy requirement of approximately 47.6–62.6 kWh kg^{-1} H_2. This additional contribution should not be included when the alkali is effectively recovered or supplied as a low-value residual stream. By comparison, acidic ER requires the above-mentioned 26–37 kWh kg^{-1} H_2 at the electrochemical stage and does not involve the stoichiometric consumption of externally supplied alkali. Although additional energy may be required when acidic ER relies on deionized or reverse-osmosis water, the energy demand for water purification is typically low (<1 kWh m^{-3}) [61,62] compared with the electrochemical energy requirements and the energy associated with NaOH regeneration. Therefore, this contribution is not expected to significantly affect the overall energy balance (see Figure 1).

Economics

Ethanol ER provides a representative case study for comparing acidic and alkaline architectures, although many of the underlying economic considerations also apply to other bioalcohols. A meaningful comparison must account simultaneously for operating costs, capital requirements, downstream separation and coproduct value.

Although alkaline ethanol ER may offer favourable kinetics and broader catalyst compatibility, these advantages can be offset by the stoichiometric consumption of base. On-site chloro-alkali NaOH production requires an estimated additional 21–36 kWh, corresponding to approximately $1.05–3.60 per kg of H_2 at industrial electricity prices of $0.05–0.10/kWh [63]. This recurring cost may rapidly exceed the one-time materials premium of acidic systems.

Table 3

Energetics for producing 1 kg of H_2 in acid and alkaline ethanol ER.

Reference	Membrane and pH	Catalysts (cathode, anode)	T (°C)	Current density (mA/cm^2)	H_2 Production energy (kWh/kgH_2)	Faradic efficiency	Biomass oxidation products
Calcerrada et al. [57]	Nafion, acid	Pt–Sn/C	50	100 (1V)	29.75 to ~37.2	99%	Acetic acid
Lamy et al. [55]	Nafion, acid	Pt–Sn–Ru	20	100	25.6	96%[b]	Acetic acid
Lo Vecchio et al. [56]	Nafion, acid	Pt–Ru	90	940 (1V)	26.6[a]	Not reported	Acetic acid (mixed pathway)
Zhang et al. [54]	Membraneless, alkaline	Au–Cu/C	NA	1A/mg of metal (1.05V)	27.9[a]	>92%	Sodium Acetate
Chen et al. [21]	Tokuyama A201, alkaline	Pd/TiO_2 nanotubes	80	1 A/cm^2 (0.92V) (0.69V)	24,66 18.49	Not reported	Sodium Acetate
Fu et al. [58]	Nafion211 alkaline	Pt–Cu NF/C	NA	10 mA/cm^2 (0.58V)	15.4[a]	98–99%	Sodium Acetate
Alemany Molina et al. [59]	Fumasep FAA-3-50, alkaline	Pt–Fe–N/AS	60	123 mA/cm^2 (0.9V)	23.9[a]	Not reported	Potassium Acetate

ER, electrochemical reforming; NA, not applicable; Pd/TiO_2, palladium/titanium dioxide; NF/C, non-ferrous and copper metallurgy.
[a] Estimated by the authors.
[b] Calculated from the ratio between experimentally measured and theoretical hydrogen production. Lamy et al. attributed the small deviation from unity to hydrogen leakage and/or membrane crossover rather than parasitic electrochemical reactions.

Alkaline ethanol oxidation also produces acetate rather than acetic acid, requiring either downstream acidification with sulfuric acid (H_2SO_4) and associated salt-waste generation or acceptance of a potentially lower-value product. Although product distributions vary with substrate and catalyst, similar constraints may arise for other bioalcohols and biomass-derived polyols, for which alkaline oxidation generally yields carboxylate salts rather than free acids.

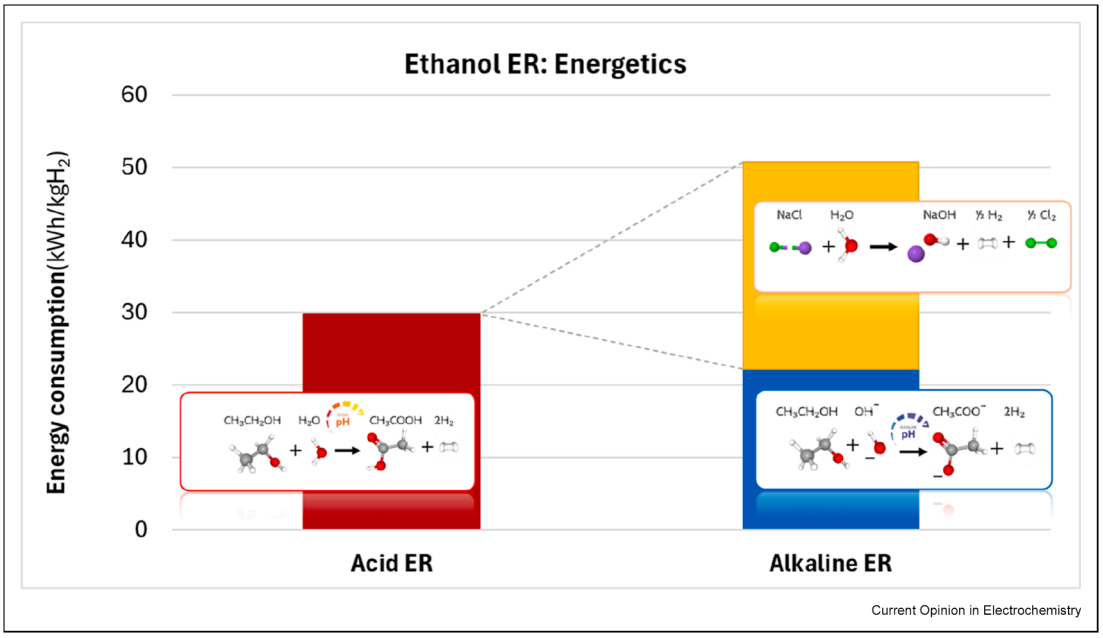
The capital burden of acidic PEM systems may therefore be less severe at the system level than commonly assumed. Based on recent market values of approximately \$50.80/g Pt and \$49.03/g Ru, a total Pt—Ru loading of 2 mg cm^{-2} over 100 cm^2 corresponds to a raw-metal cost of approximately \$10 per cell. Adding an estimated \$5—8 for the Nafion membrane brings the upfront materials' cost to approximately \$15—18 per cell, excluding catalyst preparation, deposition, gas-diffusion layers and manufacturing. This expenditure is comparable to the estimated NaOH penalty associated with producing approximately 4—14 kg of H_2 under alkaline conditions. Over moderate operating lifetimes, the apparent cost disadvantage of PGM-based acidic cells may therefore become less significant.

Acidic ethanol ER also directly produces acetic acid, potentially simplifying product recovery and enabling a biorefinery configuration, in which both hydrogen and the organic coproduct contribute to revenue. The same principle may extend to other bioalcohols when oxidation yields marketable free acids, although selectivity and product value remain strongly substrate-dependent and catalyst-dependent.

Separation costs further affect the comparison. In alkaline ethanol ER, acetate recovery from dilute alkaline streams may require bipolar-membrane electrodialysis or related technologies, with reported energy demands of 7.4—22.3 kWh per kilogram of recovered acetic acid [64]. These costs may be reduced in acidic ER, where the free acid is formed directly. Alkaline systems can also employ non-noble-metal catalysts [42,43], although AEM durability remains a concern, with conductivity losses of 30—50% reported after 500 h [49]. More broadly, scale-up studies of low-loading alkaline devices indicate that reductions in noble-metal content and balance-of-plant optimisation can substantially improve system economics [65]. While these results are not directly transferable to ethanol ER, they illustrate the potential advantages of catalyst minimisation and engineering at scale.

Ethanol should therefore be viewed as a case study rather than a unique exception. The broader relevance of this framework is illustrated by the techno-economic analysis of Sibal et al. on crude glycerol electrooxidation. Crude glycerol is generated as a low-value byproduct of

Figure 1



Energy consumption associated with ethanol ER under acidic and alkaline conditions based on data in Table 1. In acidic ER, hydrogen production coupled with ethanol oxidation to acetic acid requires an average of ~30 kWh kg^{-1} H_2 at the electrochemical stage. In alkaline ER, the electrochemical demand (average ~22 kWh kg^{-1} H_2) is lower due to more favourable reaction kinetics. However, when the energy required to regenerate NaOH via the chlor-alkali process is included, the total alkaline system energy demand increases to ~50 kWh kg^{-1} H_2. ER, electrochemical reforming.

biodiesel production, making its electrochemical valorisation particularly relevant to integrated biorefineries. Their analysis showed that economic feasibility depends strongly on feedstock purity, electricity prices and assumptions regarding the value of the oxidised products [7].

Overall, neither acidic nor alkaline ER has a universal economic advantage. For ethanol and other high-added-value chemicals, the balance depends on base consumption, electricity prices, catalyst and membrane lifetime, separation requirements, feedstock origin, product markets and operating scale. The practical suitability of acidic and alkaline electroreforming will also depend on the nature and composition of the available industrial residual stream. Acidic systems may be particularly attractive for waste-derived or fermented bioethanol streams, whose feasibility under realistic feed conditions has already been demonstrated, especially when the direct production of free carboxylic acids is desirable, and downstream neutralisation should be minimised [3]. Conversely, alkaline electroreforming may be advantageous when the feed is already available in an alkaline matrix, when caustic streams are generated as low-value byproducts in adjacent industrial processes or when the corresponding carboxylate salts can be directly used or recovered without acidification. High-performance alkaline electroreforming has already been demonstrated for biomass-derived alcohols, supporting the potential of this configuration when hydroxide-rich feeds and carboxylate products are compatible with the intended process scheme [21]. Crude glycerol from biodiesel production represents one of the most relevant industrial examples, as its electrochemical valorisation has been demonstrated using industrially sourced streams and assessed from both techno-economic and life-cycle perspectives [7,12]. Other promising candidates include lignocellulosic hydrolysates and biomass-derived feeds containing glucose or lignin-derived compounds, although their greater compositional complexity may increase pretreatment requirements and the risk of catalyst deactivation [4–6]. In all cases, impurities, water content, salt concentration, feed alkalinity, catalyst poisoning, pretreatment requirements, desired product form, product value and downstream separation costs must be evaluated case by case before selecting an acidic or alkaline configuration.

Conclusion

In the opinion of the authors, the path to commercial bioalcohols' ER may probably require a focus on acidic systems, reducing costs while improving durability and process intensity. Specific priorities include: (i) ultra-

low-loading PGM architectures (sub-0.5 mg cm^{-2}) to minimise precious metal costs, (ii) hydrocarbon-based PEMs (cost target <\$100/m^2) to replace expensive perfluorinated ionomers while maintaining conductivity and stability, (iii) ionomer-free electrode designs that reduce both catalyst and polymer requirements and (iv) advanced cell architectures (flow-through reactors, intensified mass transport) that enable operation at lower catalyst loadings without sacrificing current density. Alkaline ER retains niche applicability in scenarios where sodium acetate or other carboxylate salts have direct market value, where on-site NaOH is available as a waste stream from adjacent processes or where complete oxidation to carbonate for waste treatment is acceptable. However, for mainstream biorefinery applications targeting simultaneous green hydrogen and valuable chemical production, acidic systems may offer better techno-economic viability than alkaline ER.

Finally, although this opinion has focused on the energy balance of acidic and alkaline electroreforming, future studies should increasingly validate these technologies using realistic industrial residual streams rather than model compounds. The choice of feedstock, including its composition, impurities and pretreatment requirements, is expected to play an important role in determining the practical viability of each approach and therefore deserves dedicated investigation.

CRediT authorship contribution statement

I.P., **A.L.:** Conceptualisation. **I.P.**, **M.V.P.**, **M.B.**, **A.L.**: Formal analysis. **I.P.:** Investigation. **M.B.**, **A.L.:** Funding acquisition. **I.P.**, **A.L.:** Methodology. **A.L.:** Project administration. **A.L.:** Supervision. **I.P.**, **M.B.**, **M.V.P**, **A.L.:** Validation. **I.P.**, **E.B.:** Visualisation. **I.P.:** Writing – original draft; **I.P.**, **E.B.**, **M.V.P.**, **M.B.**, **A.L.:** Writing – review and editing.

Funding sources

A.L. thanks the project 'Mission Innovation' Poa 2021–2023. Hydrogen Demo Valley: Infrastrutture Polifunzionali Per La Sperimentazione E Dimostrazione Delle Tecnologie Dell'idrogeno La 2.7 (transl. Hydrogen Demo Valley: Multifunctional Infrastructures for the Experimentation and Demonstration of Hydrogen Technologies, Line 27) funded by the Italian Ministero dell'Ambiente e della Sicurezza energetica (transl. Italian Ministry of the Environment and Energy Security) (MASE).

Declaration of competing interest

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

Data availability

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

References

Papers of particular interest, published within the period of review, have been highlighted as:

* of special interest
** of outstanding interest

1. Kahlstorf T, Hausmann JN, Sontheimer T, Menezes PW: **Challenges for hybrid water electrolysis to replace the oxygen evolution reaction on an industrial scale**. *Glob Chall* 2023, **7**, 2200242, https://doi.org/10.1002/gch2.202200242.

2. ** Wang G, Chen A, Chen Y, *et al.*: **Advancements in electrochemical synthesis: expanding from water electrolysis to dual-value-added products**. *eScience* 2025, **5**, 100333, https://doi.org/10.1016/j.esci.2024.100333.
This review provides a comprehensive overview of the transition from conventional water electrolysis towards hybrid electrolysis systems capable of simultaneously producing hydrogen and value-added chemicals. It systematically compares anodic organic oxidation strategies, catalyst design principles and techno-economic perspectives, highlighting dual-value-added electrolysis as a promising route for industrial decarbonisation.

3. Serrano-Jiménez J, de la Osa AR, Rodríguez-Gómez A, Sánchez P, Romero A, de Lucas-Consuegra A: **Electroreforming of bioethanol produced by sugar fermentation on a Pt-Ni anodic catalyst supported on graphene nanoplatelets**. *J Environ Chem Eng* 2023, **11**, 109703, https://doi.org/10.1016/j.jece.2023.109703.

4. Liu WJ, Xu Z, Zhao D, *et al.*: **Efficient electrochemical production of glucaric acid and H2 via glucose electrolysis**. *Nat Commun* 2020, **11**:265, https://doi.org/10.1038/s41467-019-14157-3.

5. Du X, Zhang H, Sullivan KP, Gogoi P, Deng Y: **Electrochemical lignin conversion**. *ChemSusChem* 2020, **13**:4318–4343, https://doi.org/10.1002/cssc.202001187.

6. Bi J, Bai W, Zhang J, Gong L, Dou S: **Recent advances in electrocatalytic lignin valorization: mechanism-oriented design of selective bond-breaking catalysts**. *ChemSusChem* 2026, **19**, e202502756, https://doi.org/10.1002/cssc.202502756.

7. ** Sibal AP, Gaines RN, Friel BE, Kenis PJA, Stillwell AS: **Turning waste into value: technoeconomic analysis and life cycle assessment of biodiesel-derived crude glycerol electrooxidation**. *Environ Sci Technol* 2026, **60**:5492–5504, https://doi.org/10.1021/acs.est.5c16857.
This work combines techno-economic analysis and life-cycle assessment to evaluate waste-derived feedstock electrooxidation as a sustainable strategy for hydrogen production and chemical valorisation. The major contribution of the study lies in demonstrating the environmental and economic feasibility of integrating biomass-derived organics into industrial electrolysis systems.

8. Guo L, Shui S, Zhang L, *et al.*: **Recent developments in electrocatalytic oxidation of glycerol for value-added products synthesis**. *Nanotechnology* 2025, **37**, 012003, https://doi.org/10.1088/1361-6528/ae2a38.

9. Dimos MM, Blanchard GJ: **Electro-catalytic oxidation of 1,2-propanediol at nanoporous and planar solid Pt electrodes**. *J Electroanal Chem* 2011, **654**:13–19, https://doi.org/10.1016/j.jelechem.2011.01.042.

10. ** van Lieshout F, Castañeda-Morales E, Manzo-Robledo A, Morales DM: **Electrooxidation of alcohols under the operating conditions of industrial alkaline water electrolysis**. *Ind Chem Mater* 2026, **4**:7–32, https://doi.org/10.1039/D5IM00071H.
This work investigates alcohol electrooxidation under industrial alkaline electrolysis conditions, providing valuable insight into catalyst performance, reaction kinetics and operational constraints at commercially relevant current densities and temperatures. The study is particularly relevant for assessing the practical integration of biomass electroreforming into existing alkaline electrolyser platforms.

11. Chadderdon DJ, Xin L, Qi J, *et al*.: **Selective oxidation of 1,2-Propanediol in alkaline anion-exchange membrane electrocatalytic flow reactors: experimental and DFT investigations**. *ACS Catal* 2015, **5**:6926–6936, https://doi.org/10.1021/acscatal.5b01085.

12. Gaines RN, Sibal AP, Bradley AM, *et al*.: **Electrolysis for valorization of industrially-sourced crude glycerol**. *ACS Sustainable Chem Eng* 2025, **13**:13250–13260, https://doi.org/10.1021/acssuschemeng.5c03028.

13. Pagliaro MV, Bruni F, Oberhauser W, *et al*.: **Hydrogen and high-value-added chemicals from glycerol electroreforming using a highly efficient and selective ligand-stabilized PdCu catalyst**. *ACS Sustainable Chem Eng* 2025, **13**:4975–4987, https://doi.org/10.1021/acssuschemeng.4c09284.

14. Yan Y, Hao P, Fu Y, *et al*.: **Selective electrooxidation glycerol to lactic acid coupled with hydrogen production over a cooperative BiOx/Au catalyst**. *AIChE J* 2024, **70**, e18370, https://doi.org/10.1002/aic.18370.

15. ** Luo H, Xu M, Liu S, *et al*.: **Selective glycerol to lactic acid conversion via a tandem effect between platinum and metal oxides with abundant acid groups**. *EES Catal* 2025, **3**:87–96, https://doi.org/10.1039/D4EY00236A.
This study reports a tandem catalytic strategy for the selective electrooxidation of glycerol to lactic acid using platinum and acid-functionalised metal oxides. The work highlights how catalyst–support interactions and surface acid sites can steer biomass-derived alcohol oxidation towards high-value products with enhanced selectivity and efficiency.

16. Shen L, Sun L, Douthwaite M, Akdim O, Taylor S, Hutchings GJ: **Hollow Au1Cu1(111) bimetallic catalyst promotes the selective electrochemical conversion of glycerol into glycolic acid**. *ACS Catal* 2024, **14**:11343–11351, https://doi.org/10.1021/acscatal.4c00483.

17. Tuleushova N, Holade Y, Cornu D, Tingry S: **Glycerol electroreforming in alkaline electrolysis cells for the simultaneous production of value-added chemicals and pure hydrogen – mini-review**. *Electrochem Sci Adv* 2023, **3**, e2100174, https://doi.org/10.1002/elsa.202100174.

18. Sun Y, Miao J, Fan X, Zhang K, Zhang T: **Recent progress in electrochemical conversion from biomass derivatives into high-value-added chemicals**. *Small Struct* 2024, **5**, 2300576, https://doi.org/10.1002/sstr.202300576.

19. * Muhyuddin M, Santoro C, Osmieri L, *et al*.: **Anion-exchange-membrane electrolysis with alkali-free water feed**. *Chem Rev* 2025, **125**:6906–6976, https://doi.org/10.1021/acs.chemrev.4c00466.
This review discusses the emerging field of alkali-free anion-exchange-membrane (AEM) electrolysis, addressing membrane chemistry, catalyst stability, ion transport and device engineering. The article is highly significant because it identifies the key scientific and technological barriers limiting industrial deployment of safer and more sustainable alkaline-free electrolysis systems.

20. Berretti E, Osmieri L, Baglio V, *et al*.: **Direct alcohol fuel cells: a comparative review of acidic and alkaline systems**. *Electrochem Energy Rev* 2023, **6**:30, https://doi.org/10.1007/s41918-023-00189-3.

21. Chen YX, Lavacchi A, Miller HA, *et al*.: **Nanotechnology makes biomass electrolysis more energy efficient than water electrolysis**. *Nat Commun* 2014, **5**:4036, https://doi.org/10.1038/ncomms5036.

22. Wei RL, Sun YN, Liu Y, Cai WB, Yang YY: **Which catalyst exhibits superior C–C bond cleavage ability in ethanol electrooxidation: an In-Situ ATR-SEIRAS investigation**. *J Am Chem Soc* 2026, **148**:9185–9191, https://doi.org/10.1021/jacs.5c20407.

23. Campeggio J, Giurlani W, Pagliai M, Innocenti M, Fontanesi C, Chelli R: **Insights into the rate-determining step of the ethanol electro-oxidation reaction on the Pd(111) surface through Ab initio molecular dynamics simulations**. *J Phys Chem C* 2023, **127**:21075–21084, https://doi.org/10.1021/acs.jpcc.3c04587.

24. Altarawneh RM, Pickup PG: **Product distributions and efficiencies for ethanol oxidation in a proton exchange membrane electrolysis cell**. *J Electrochem Soc* 2017, **164**:F861–F865, https://doi.org/10.1149/2.0051709jes.

25. Akhmedov MA, Khidirov SS: **Electrocatalytic oxidation of ethanol on the platinum electrode in solution of methanesulfonic acid**. *Russ J Electrochem* 2022, **58**:482–489, https://doi.org/10.1134/S1023193522060039.

26. Guo Y, Li B, Shen S, Luo L, Wang G, Zhang J: **Potential-dependent mechanistic study of ethanol electro-oxidation on palladium**. *ACS Appl Mater Interfaces* 2021, **13**:16602–16610, https://doi.org/10.1021/acsami.1c04513.

27. Lamy C, Coutanceau C, Baranton S: **Chapter two - principle of hydrogen production by electrocatalytic oxidation of organic compounds in a proton exchange membrane electrolysis cell**. In *Production of clean hydrogen by electrochemical reforming of oxygenated organic compounds*. Edited by Lamy C, Coutanceau C, Baranton S, Academic Press; 2020:7–20, https://doi.org/10.1016/B978-0-12-821500-5.00002-3.

28. Lamy C, Coutanceau C, Baranton S: **Chapter four - production of hydrogen by the electrocatalytic oxidation of low-weight compounds (HCOOH, MeOH, EtOH)**. In *Production of clean hydrogen by electrochemical reforming of oxygenated organic compounds*. Edited by Lamy C, Coutanceau C, Baranton S, Academic Press; 2020:37–79, https://doi.org/10.1016/B978-0-12-821500-5.00004-7.

29. Wang L, Bevilacqua M, Chen YX, *et al*.: **Enhanced electrooxidation of alcohols at electrochemically treated polycrystalline palladium surface**. *J Power Sources* 2013, **242**:872–876, https://doi.org/10.1016/j.jpowsour.2013.06.068.

30. de Souza JPI, Queiroz SL, Bergamaski K, Gonzalez ER, Nart FC: **Electro-oxidation of ethanol on Pt, Rh, and PtRh electrodes. A study using DEMS and in-Situ FTIR techniques**. *J Phys Chem B* 2002, **106**:9825–9830, https://doi.org/10.1021/jp014645c.

31. D'Villa-Silva M, Simões FC, De Souza RFB, Silva JCM, Santos MC. In *Comparative studies of oxygen reduction reaction and ethanol oxidation reaction on PtSn/C and PtNi/C catalysts*, vol. 41; 2011:1299–1306, https://doi.org/10.1149/1.3635661.

32. Frusteri F, Freni S, Chiodo V, *et al*.: **Steam reforming of bio-ethanol on alkali-doped Ni/MgO catalysts: hydrogen production for MC fuel cell**. *Appl Catal Gen* 2004, **270**:1–7, https://doi.org/10.1016/j.apcata.2004.03.052.

33. Christensen PA, Jones SWM, Hamnett A: **In situ FTIR studies of ethanol oxidation at polycrystalline Pt in alkaline solution**. *J Phys Chem C* 2012, **116**:24681–24689, https://doi.org/10.1021/jp308783y.

34. Figueiredo MC, Arán-Ais RM, Climent V, Kallio T, Feliu JM: **Evidence of local pH changes during ethanol oxidation at Pt electrodes in alkaline media**. *Chemelectrochem* 2015, **2**:1254–1258, https://doi.org/10.1002/celc.201500151.

35. Pagliaro MV, Bellini M, Bevilacqua M, *et al*.: **Carbon supported Rh nanoparticles for the production of hydrogen and chemicals by the electroreforming of biomass-derived alcohols**. *RSC Adv* 2017, **7**:13971–13978, https://doi.org/10.1039/C7RA00044H.

36. Chen YX, Lavacchi A, Miller HA, *et al*.: **Nanotechnology makes biomass electrolysis more energy efficient than water electrolysis**. *Nat Commun* 2014, **5**:4036, https://doi.org/10.1038/ncomms5036.

37. Li L, Wong SS: **Ultrathin metallic nanowire-based architectures as high-performing electrocatalysts**. *ACS Omega* 2018, **3**:3294–3313, https://doi.org/10.1021/acsomega.8b00169.

38. Liu D, Lv Q, Zheng D, *et al*.: **Rhodium-based electrocatalysts for ethanol oxidation reaction: mechanistic insights, structural engineering, and performance optimization**. *Catalysts* 2026, **16**:114, https://doi.org/10.3390/catal16020114.

39. Bishnoi P, Mishra K, Sen U, Siwal SS: **Electrocatalytic performance in direct ethanol fuel cells: contributions of monometallic, bimetallic, and trimetallic catalysts**. *Mater Today Catal* 2025, **11**, 100124, https://doi.org/10.1016/j.mtcata.2025.100124.

40. Lo Vecchio C, Mosca E, Trocino S, Baglio V: **Investigation of an ethanol electroreforming cell based on a Pt1Ru1/C catalyst at the anode**. *Catalysts* 2024, **14**:415, https://doi.org/10.3390/catal14070415.

41. Zhang Z, Fu H, Chen C, *et al*.: **Defect-rich Pt-Ru metallic aerogels for highly efficient ethanol oxidation reaction**. *Appl Surf Sci* 2024, **652**, 159277, https://doi.org/10.1016/j.apsusc.2023.159277.

42. Berretti E, Osmieri L, Baglio V, *et al*.: **Direct alcohol fuel cells: a comparative review of acidic and alkaline systems**. *Electrochem Energy Rev* 2023, **6**:30, https://doi.org/10.1007/s41918-023-00189-3.

43. Kutyła D, Nakajima K, Fukumoto M, Wojnicki M, Kołczyk-Siedlecka K: **Electrocatalytic performance of ethanol oxidation on Ni and Ni/Pd surface-decorated porous structures obtained by molten salts deposition/dissolution of Al-Ni alloys**. *Int J Mol Sci* 2023, **24**:3836, https://doi.org/10.3390/ijms24043836.

44. Kusoglu A, Weber AZ: **New insights into perfluorinated sulfonic-acid ionomers**. *Chem Rev* 2017, **117**:987–1104, https://doi.org/10.1021/acs.chemrev.6b00159.

45. Kidwai Mazaahir, Chauhan Ritika, Bhatnagar Shilpi: **Nafion-H®: a versatile catalyst for organic synthesis**. *Curr Org Chem* 2015, **19**:72–98, https://doi.org/10.2174/1385272819666141205234539.

46. Yano H, Uematsu T, Omura J, Watanabe M, Uchida H: **Effect of adsorption of sulfate anions on the activities for oxygen reduction reaction on nafion®-coated Pt/carbon black catalysts at practical temperatures**. *J Electroanal Chem* 2015, **747**:91–96, https://doi.org/10.1016/j.jelechem.2015.04.007.

47. von Tettau P, Thiele P, Mauermann P, Wick M, Tinz S, Pischinger S: **Per- and polyfluoroalkyl substances in proton exchange membrane fuel cells — a review**. *J Power Sources* 2025, **630**, 236104, https://doi.org/10.1016/j.jpowsour.2024.236104.

48. Fenton SE, Ducatman A, Boobis A, *et al*.: **Per- and polyfluoroalkyl substance toxicity and human health review: current state of knowledge and strategies for informing future research**. *Environ Toxicol Chem* 2021, **40**:606–630, https://doi.org/10.1002/etc.4890.

49. Mustain WE, Chatenet M, Page M, Kim YS: **Durability challenges of anion exchange membrane fuel cells**. *Energy Environ Sci* 2020, **13**:2805–2838, https://doi.org/10.1039/D0EE01133A.

50. Caravaca A, Sapountzi FM, de Lucas-Consuegra A, Molina-Mora C, Dorado F, Valverde JL: **Electrochemical reforming of ethanol–water solutions for pure H2 production in a PEM electrolysis cell**. *Int J Hydrogen Energy* 2012, **37**:9504–9513, https://doi.org/10.1016/j.ijhydene.2012.03.062.

51. Kaur J, Gupta RK, Kumar A: **Electrocatalytic ethanol oxidation reaction: recent progress, challenges, and future prospects**. *Discover Nano* 2024, **19**:137, https://doi.org/10.1186/s11671-024-04067-9.

52. Li Z, Yan Y, Xu SM, *et al*.: **Alcohols electrooxidation coupled with H2 production at high current densities promoted by a cooperative catalyst**. *Nat Commun* 2022, **13**:147, https://doi.org/10.1038/s41467-021-27806-3.

53. Zhao G, Lin J, Lu M, *et al*.: **Potential cycling boosts the electrochemical conversion of polyethylene terephthalate-derived alcohol into valuable chemicals**. *Nat Commun* 2024, **15**:8463, https://doi.org/10.1038/s41467-024-52789-2.

54. * Zhang Y, Zhu W, Fang J, *et al*.: **Electrochemical converting ethanol to hydrogen and acetic acid for large scale green hydrogen production**. *Nano Res* 2024, **17**:1542–1551, https://doi.org/10.1007/s12274-023-6023-1.
This study demonstrates an efficient ethanol electroreforming strategy for the simultaneous production of hydrogen and acetic acid: it highlights the potential of replacing the oxygen evolution reaction (OER) with ethanol oxidation to significantly reduce cell voltage while generating commercially valuable coproducts.

55. Lamy C, Jaubert T, Baranton S, Coutanceau C: **Clean hydrogen generation through the electrocatalytic oxidation of ethanol in a Proton Exchange Membrane Electrolysis Cell (PEMEC): effect of the nature and structure of the catalytic anode**. *J Power Sources* 2014, **245**:927–936, https://doi.org/10.1016/j.jpowsour.2013.07.028.

56. Lo Vecchio C, Mosca E, Trocino S, Baglio V: **Investigation of an ethanol electroreforming cell based on a Pt1Ru1/C catalyst at the anode**. *Catalysts* 2024, **14**, https://doi.org/10.3390/catal14070415.

57. Calcerrada AB, de la Osa AR, Llanos J, Dorado F, de Lucas-Consuegra A: **Hydrogen from electrochemical reforming of ethanol assisted by sulfuric acid addition**. *Appl Catal B Environ* 2018, **231**:310–316, https://doi.org/10.1016/j.apcatb.2018.03.028.

58. Fu H, Zhang N, Lai F, *et al*.: **Surface-regulated platinum–copper nanoframes in electrochemical reforming of ethanol for efficient hydrogen production**. *ACS Catal* 2022, **12**:11402–11411, https://doi.org/10.1021/acscatal.2c03022.

59. * Alemany-Molina G, Mosca E, Lo Vecchio C, *et al*.: **Efficient biomass-derived catalysts for alkaline short-chain alcohols electroreforming: a focus on low platinum loading**. *J Power Sources* 2025, **631**, 236298, https://doi.org/10.1016/j.jpowsour.2025.236298.
This publication presents biomass-derived catalysts for alkaline electroreforming of short-chain alcohols, including ethanol, while minimising platinum loading. It addresses catalyst cost reduction and sustainability challenges, both critical for large-scale implementation of ethanol electroreforming technologies.

60. Kumar A, Du F, Lienhard JHV: **Caustic soda production, energy efficiency, and electrolyzers**. *ACS Energy Lett* 2021, **6**:3563–3566, https://doi.org/10.1021/acsenergylett.1c01827.

61. Tigrine Z, Aburideh H, Zioui D, *et al*.: **Feasibility study of a reverse osmosis desalination unit powered by photovoltaic panels for a sustainable water supply in Algeria**. *Sustainability* 2023, **15**, 14189, https://doi.org/10.3390/su151914189.

62. Porada S, Zhang L, Dykstra JE: **Energy consumption in membrane capacitive deionization and comparison with reverse osmosis**. *Desalination* 2020, **488**, 114383, https://doi.org/10.1016/j.desal.2020.114383.

63. Kotowicz J, Baszczeńska O, Niesporek K: **Cost of green hydrogen**. *Energies* 2024, **17**:4651, https://doi.org/10.3390/en17184651.

64. Xue S, Wu C, Wu Y, Zhang C: **An optimized process for treating sodium acetate waste residue: coupling of diffusion dialysis or electrodialysis with bipolar membrane electrodialysis**. *Chem Eng Res Des* 2018, **129**:237–247, https://doi.org/10.1016/j.cherd.2017.11.013.

65. Zappia MI, Bellani S, Zuo Y, *et al*.: **High-current density alkaline electrolyzers: the role of Nafion binder content in the catalyst coatings and techno-economic analysis**. *Front Chem* 2022, **10**. 2022, https://www.frontiersin.org/journals/chemistry/articles/10.3389/fchem.2022.1045212.