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Fundamentals and Advantages of Hybrid Water Electrolysis

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1.1 Concept and Scope

Conventional low-temperature water electrolysis relies on two coupled half-reactions: hydrogen evolution reaction (HER) at the cathode and oxygen evolution reaction (OER) at the anode. The corresponding reactions in alkaline and acidic media are shown in Eqs. (1.1)–(1.6) [1]:

alkaline media

$$\text{cathode (HER)} : 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (1.1)$$

$$\text{anode(OER)} : 4OH^- \rightarrow O_2 + 2H_2O + 4e^- \quad (1.2)$$

$$\text{overall} : 2H_2O \rightarrow 2H_2 + O_2 \quad (1.3)$$

acidic media

$$\text{cathode (HER)} : 2H^+ + 2e^- \rightarrow H_2 \quad (1.4)$$

$$\text{anode (OER)} : 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (1.5)$$

$$\text{overall} : 2H_2O \rightarrow 2H_2 + O_2 \quad (1.6)$$

HER can be accelerated across a wide range of catalyst classes [2, 3]. In contrast, OER is the dominant efficiency bottleneck in most practical electrolyzers because it involves multi-electron transfer, multiple adsorbed intermediates, and intrinsically sluggish kinetics, which together result in large overpotentials and substantial

energy losses [4, 5]. In Figure 1.1a, a conceptual layout of a hybrid electrolyzer that retains HER while modifying the anodic reaction is shown.

Hybrid water electrolysis is based on a straightforward yet far-reaching modification. The anode is redesigned to partially or fully replace OER with an alternative anodic oxidation reaction (AOR), while HER remains the cathodic reaction responsible for hydrogen production [6, 7]. Electrons generated by anodic oxidation flow through the external circuit to drive HER. Charge-compensating ionic species, i.e., OH^- in alkaline or anion-exchange membrane systems, move through the electrolyte or membrane between compartments (Figure 1.1b). When AOR is chosen over OER due to its lower thermodynamic potential and more favorable kinetics, the anode can operate at a lower potential. This approach lowers the full cell voltage required to reach a given current density, thus enhancing the overall electricity-to-hydrogen efficiency [8].

In the literature, several terms are used to describe closely related concepts, including hybrid water electrolysis [9], assisted water electrolysis [10], paired electrolysis [11], and electrochemical reforming [12]. These notions overlap but are not identical. In this chapter, hybrid water electrolysis is defined as an electrolysis

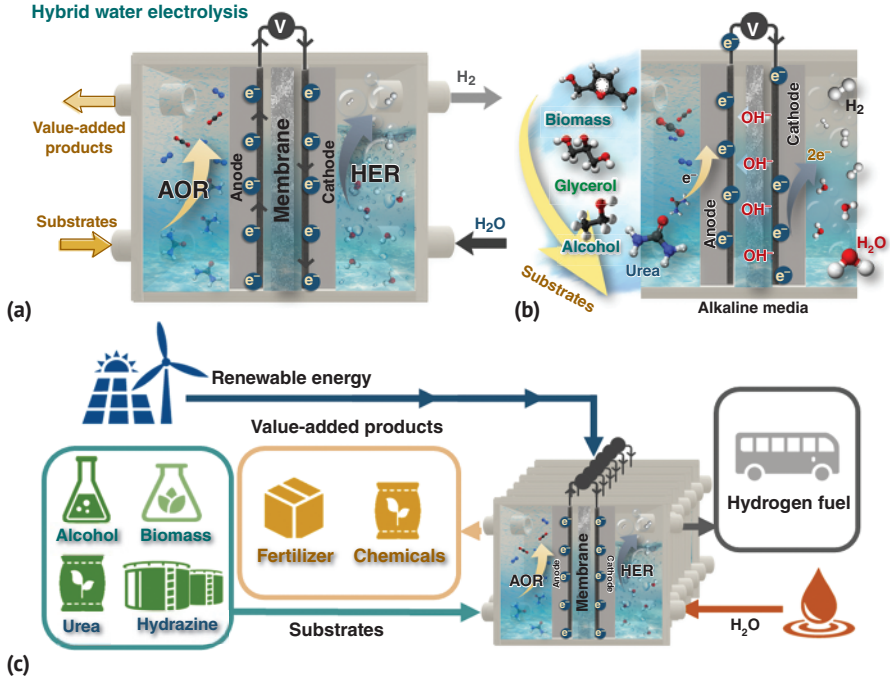

Figure 1.1 Schematic illustration of hybrid water electrolysis: (a) hybrid electrolyzer in which HER is coupled with AOR that replaces OER; (b) charge and species transport showing electron flow through the external circuit and ion transport through the electrolyte or membrane, e.g., OH^- in alkaline or anion-exchange membrane systems, with separated product streams; and (c) process outputs emphasizing the dual-function anode: hydrogen generation at the cathode and selective formation of value-added chemicals and/or treated effluent at the anode, depending on the chosen substrate.

configuration that couples HER with AOR. To reduce the cell voltage relative to conventional OER-driven water splitting, an AOR is selected, enabling the formation of functional anodic products such as value-added chemicals or detoxified waste-derived species [13]. This definition underscores the anode as an active chemical conversion module rather than merely an oxygen generator. It further emphasizes that both hydrogen production and the fate of the anodic substrate must be taken into account when assessing performance. In Figure 1.1c, the dual-output nature of the process is illustrated, with hydrogen produced at the cathode and value-added products or treated effluent generated at the anode.

Hybrid electrolysis can be viewed at three nested levels: reaction pairing, electrode function, and system design. At the reaction level, the core feature is a coupled pair in which cathodic HER consumes electrons supplied via an external circuit, and anodic oxidation supplies electrons by oxidizing a chosen substrate. At the electrode-function level, the anode is no longer optimized solely for OER stability. It must regulate adsorption, dehydrogenation, oxygen insertion, and often C—C or C—O bond transformations, with selectivity serving as a central metric. At the system level, the electrolyte, membrane (if present), electrode architecture, and operating mode (batch, flow-through, fed-batch, or continuous) must accommodate organic feed and product streams, including their transport, crossover tendencies, and downstream recovery requirements. Given the strong interactions among these layers, hybrid electrolysis is best regarded as a coupled electrochemical–chemical process rather than a minor variant of conventional water splitting.

The practical motivation for hybrid electrolysis extends beyond voltage reduction, although this is often the most visible advantage. A defining attribute is the ability to coproduce chemicals with a value greater than that of oxygen. Anodic oxidation of alcohols can yield aldehydes, carboxylic acids, or other oxygenates, while oxidation of primary amines can be directed toward nitriles under suitable catalytic environments [14, 15]. Certain substrates are also attractive because they are abundant in waste streams, such as urea-containing wastewater, which permits simultaneous hydrogen production and wastewater treatment or pollutant abatement [16].

The anodic reaction space is broad and includes urea [17], alcohols and polyols [18, 19], amines [20], and other organics, as well as biomass-derived molecules [21] and complex waste streams [22]. Within this space, thermodynamic advantages are often shown using representative potentials, as shown in Figure 1.2a. Urea oxidation has a markedly lower theoretical oxidation potential (about 0.37 V vs. RHE) than OER (1.23 V vs. RHE), and carbon oxidation has been proposed to yield even lower values in some conceptual schemes [23]. Reports of very low operating cell voltages in small-molecule systems demonstrate the magnitude of voltage reduction achievable when the anodic reaction proceeds efficiently, and competing OER is suppressed [24, 25]. At the same time, these values should be treated as indicators of feasibility rather than guarantees of device performance, because kinetic barriers, mass transport, and parasitic reactions often govern the observed voltage at practical current densities.

Such considerations motivate the scope boundaries adopted here. First, hybrid electrolysis is not defined by the mere presence of an organic molecule in

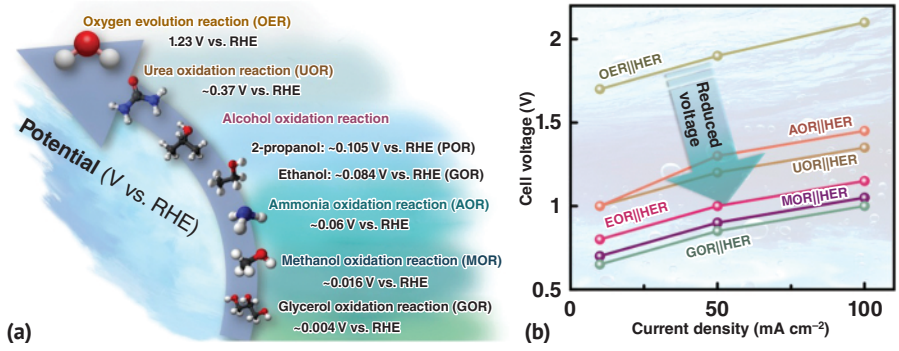

Figure 1.2 Thermodynamic and kinetic basis for energy reduction in hybrid electrolysis: (a) qualitative comparison of equilibrium potentials vs. RHE, highlighting that many AORs have lower thermodynamic potentials than OER, thereby reducing the minimum reversible cell voltage when paired with HER; and (b) schematic polarization curves comparing conventional OER-coupled electrolysis with AOR-coupled operation, illustrating how reduced anodic overpotential and suppressed OER shift the operating voltage downward at a given current density.

the electrolyte. Instead, it is defined by whether the organic oxidation reaction controls anodic charge transfer in the operating regime of interest. Competing OER can reemerge at elevated potentials, particularly if anodic oxidation pathways become transport-limited, surface poisoning reduces turnover, or the catalyst preferentially stabilizes oxygen-evolution intermediates. In these cases, the apparent advantage can diminish when the current is high, and the anode output may consist of a mixture of partial-oxidation products, deep oxidation products, and oxygen. Hybrid electrolysis must be discussed in terms of faradaic partitioning. This concept shows how current divides among competing anodic pathways and why overall current density alone is not sufficient.

Second, the anode typically produces liquid-phase products, making selectivity and carbon balance key design considerations. Organic oxidation proceeds through multistep pathways involving shared intermediates. Consequently, product distributions are sensitive to potential, local pH, substrate concentration, and mass transport. A catalyst that lowers the anode potential but generates a complex product mixture may be scientifically useful yet economically unattractive if separation costs are high [26]. In contrast, systems that produce few products at high faradaic efficiency (FE) can remain attractive even when the voltage advantage is small, due to product value and ease of separation.

Third, hybrid electrolysis should be regarded as a class of electrochemical technologies. It can be applied across multiple electrolyzer configurations rather than being limited to a single type of device. Many demonstrations employ alkaline electrolytes because alkaline conditions support a wide range of non-precious catalysts and can be compatible with anion exchange membranes. However, membranes introduce additional constraints, including organic crossover, chemical compatibility, and the management of local pH and water [27]. These factors influence achievable current density, durability, and the practicality of collecting anodic products at usable concentrations.

Finally, hybrid electrolysis carries distinct safety and scalability implications. Replacing OER can reduce oxygen generation at the anode. Some schemes do not generate gaseous products, e.g., CO_2 or N_2, thereby mitigating risks associated with H_2/O_2 coexistence and gas crossover. At the same time, organic feeds introduce new safety and handling considerations, including the flammability of particular substrates and the need for proper containment and separation [28]. Successful scale-up requires maintaining selectivity, catalyst stability, and system performance at industrially relevant operating conditions.

In summary, hybrid water electrolysis is defined here as a coupled electrochemical platform that retains cathodic HER while replacing anodic OER with a strategically chosen oxidation reaction, thereby reducing energy input and generating valuable anodic products or remediation outcomes. Its scope encompasses reaction thermodynamics and kinetics, selectivity and carbon balance, and device-level integration, because the motivating advantages are realized only when these elements are optimized together.

1.2 Thermodynamic and Kinetic Basis for Energy Reduction

The central energy argument for hybrid water electrolysis is most clearly expressed by distinguishing between what is thermodynamically possible and what is kinetically achievable at practical current densities. In conventional water electrolysis, the minimum reversible voltage is set by the equilibrium potentials of HER at the cathode and OER at the anode. The operating voltage is always higher because activation, ohmic, and mass-transport losses must be overcome. Hybrid water electrolysis modifies the equilibrium requirement at the anode by replacing OER with an alternative AOR. This approach mitigates kinetic losses, as many AORs proceed through pathways that are, under appropriate conditions, less kinetically demanding than OER.

Thermodynamically, the full-cell reversible voltage is the difference between the anode and cathode equilibrium potentials with additional terms accounting for the activities of reactants and products through the Nernst equation. OER is intrinsically energy-intensive because it is linked to the oxygen or water redox couple and sets the anode equilibrium potential around 1.23 V vs. RHE under standard conditions. In contrast, many AORs exhibit much lower theoretical oxidation potentials, thus reducing the reversible voltage required to couple the anodic reaction to HER. Urea oxidation, with a theoretical oxidation potential of ~0.37 V vs. RHE, is a frequently cited example. Carbon oxidation, with a representative potential near 0.21 V vs. RHE, exemplifies the thermodynamic advantage of choosing a suitable anodic reaction.

A lower equilibrium potential does not automatically guarantee lower energy consumption in practice. At a given current density, the operating cell voltage is best understood as the sum of the reversible voltage and the losses from overpotentials and resistance. Hybrid electrolysis primarily targets the reversible anode potential and, in favorable cases, the anode activation overpotential. At high current densities,

ohmic losses and mass-transport overpotentials can dominate. Device-level demonstrations should be evaluated under practical operating conditions, rather than at low current densities where transport limitations are minimal. In Figure 1.2b, the conceptual differences between OER-coupled and AOR-coupled polarization behaviors and their impacts on operating voltage are illustrated.

The kinetic advantage of replacing OER arises from fundamental differences in reaction complexity. OER is a multistep, four-electron process that typically involves the formation and transformation of oxygenated intermediates and an O—O bond formation step, which together contribute to sluggish kinetics and large overpotential requirements. Consequently, OER typically sets the anodic overpotential and limits performance in conventional low-temperature water electrolyzers. Organic oxidation reactions involve complex, multistep pathways. When catalysts provide suitable adsorption energetics for dehydrogenation and oxygen-insertion steps, oxidation reactions can proceed at lower anode potentials. This effect is particularly evident in alkaline media, where surface hydroxyl species play a central role. At a given current density, the anodic polarization curve shifts to more negative potentials, thereby reducing the full-cell voltage required to sustain HER at the cathode.

Voltage reduction translates directly into energy savings. Under ideal conditions with 100% FE toward H_2, the production of 1 mol of hydrogen requires a charge of 2 F. The electrical energy input approximates the operating cell voltage multiplied by 2 F. Even a modest decrease in operating voltage, sustained at high current density over long periods, can substantially reduce electricity consumption.

Hybrid electrolysis shifts part of the energy demand from electricity to chemical feedstock. Organic substrates are oxidized at the anode, providing electrons and chemical energy that reduce the electrical input. This shift is intrinsic to electrochemical reforming and paired electrolysis concepts. A fair assessment distinguishes between electrical energy savings and total energy consumption. It considers the chemical energy content and cost of the feedstock as well as the economic value of the anodic products.

In particularly favorable cases, anodic oxidation is sufficiently advantageous that the required external voltage becomes very small. Reports of extremely low operating voltages in selected small-molecule systems highlight this upper bound. Some aldehyde-based systems, for example, have been reported to operate at cell voltages as low as 0.3 V. This finding illustrates how dramatically electrical input can be reduced relative to OER-driven operation when the anodic chemistry is appropriately selected and efficiently catalyzed [29].

In practice, the kinetics are more complex. Organic oxidation rarely follows a single pathway, and the observed rate depends strongly on active surface, local pH, and mass transport. Many AORs proceed through multiple dehydrogenation steps and oxygenated intermediates, so higher activity can come at the expense of selectivity [30]. Conditions that maximize current can lead to deeper oxidation or C—C cleavage. In contrast, conditions that favor selective partial oxidation may become transport-limited at high current density. The kinetic advantage over OER is not automatic. It is achieved only when catalysts sustain fast turnover rates at low anode potentials, avoid persistent poisoning, and suppress OER.

Competition between AOR and OER determines voltage reduction. Even if AOR has a lower thermodynamic potential than OER, the anode potential can still shift into a region where OER becomes significant. This shift can occur when the substrate is locally depleted, products accumulate and block active sites, or the surface reconstructs into a more OER-active state. In such a scenario, some of the anodic current produces oxygen instead of driving organic oxidation, thereby reducing both the voltage benefit and FE toward the desired products. Practical energy gain depends not only on a lower equilibrium potential but also on maintaining selectivity for organic oxidation over OER across the intended operating range.

Device configuration further influences the realization of thermodynamic and kinetic advantages. In membrane electrolyzers, such as those based on anion exchange membranes, both membrane and ionomer contribute additional ohmic resistance. They also impose constraints on water management and ion transport, which can reduce the voltage benefit of replacing OER. On the other hand, membrane separation can improve practical performance by isolating products and reducing crossover. It also enables continuous operation that stabilizes substrate supply and removes products [21]. Recent demonstrations using membrane-based or flow-through designs emphasize that coupling reaction thermodynamics with transport-aware engineering is essential for sustaining low-voltage operation at meaningful current densities.

In summary, hybrid water electrolysis reduces electrical energy input through a combination of thermodynamic and kinetic effects. Replacing OER with an AOR lowers the reversible anode potential and, under favorable catalytic conditions, can reduce activation overpotentials relative to OER. The extent of the realized benefit is determined by the total voltage loss and by competition between organic oxidation and residual OER. The most credible path to durable energy reduction is to identify a low-potential anodic reaction. This must be coupled with the design of catalysts and electrolyzer architectures that keep the anode in a regime where organic oxidation dominates charge transfer. Product formation must remain controlled, and transport limitations should not drive the system back toward OER-like operation.

1.3 Anodic Reaction Space and Substrate Selection

The anodic reaction space in hybrid water electrolysis is considerably broader than that of conventional water splitting. The anode is no longer confined to OER. Instead, it can be coupled to the oxidation of nitrogen-containing wastes, oxygenated organics, biomass-derived feeds, and other substrates. These reactions can occur at potentials lower than OER and yield products with either economic value or environmental benefit. This breadth is a core strength, but it also creates a practical challenge. Hybrid electrolysis is not a single chemistry. The most suitable substrate depends on which constraint dominates in the targeted deployment, whether electricity cost, feedstock availability, product value, separation energy, safety, or wastewater treatment needs. In Table 1.1, a structured overview of representative substrate classes, their primary value propositions, and key constraints is provided.

Table 1.1 Summary of representative substrate classes, including urea, alcohols and polyols, aldehydes, amines, and biomass-derived streams, and their primary value propositions, such as voltage reduction, chemical coproduction, or remediation.

Representative feed	Primary advantage(s)	Selectivity challenge	Main risks	Best-fit configuration(s)	Source
N-containing feeds					
Urea	Remediation/voltage	Low–med	Carbonate crossover	Alkaline AEM, flow	[31, 32]
Amines/ammonia/ ammonium	Remediation/voltage	Med	N-speciation crossover	Alkaline AEM, flow	[33, 34]
Hydrazine	Voltage	Low–med	Safety/handling crossover	Alkaline, flow (controlled)	[19, 35]
O-containing small molecules					
Alcohols (C_1–C_3)	Voltage reduction, coproduct	Med–high	Over-oxidation, OER	Alkaline, batch/flow	[21]
Polyols (e.g., glycerol)	Coproduct	High	Product mixtures, transport limits	Alkaline, flow	[27]
Aldehydes	Coproduct	High	Over-oxidation, catalyst poisoning	Alkaline (controlled), batch/flow	[36, 37]
Biomass/waste streams					
Crude glycerol	Remediation/coproduct	High	Impurities, fouling	Flow + pretreatment	[38]
Wastewater organics	Remediation	High	Variability, poisoning	Flow, robust electrodes	[21]
Biorefinery-derived feeds	Coproduct	High	Mixtures instability	Flow-controlled conditions	[39]

A useful framework for discussion is to classify anodic substrates according to their primary value proposition. The first category comprises energy-driven substrates, which are mainly employed to reduce the overall cell voltage and, consequently, the electrical energy input required for hydrogen production. Urea represents a canonical example, as its theoretical oxidation potential is significantly lower than that of OER. This thermodynamic advantage can translate into substantial voltage reductions when urea oxidation dominates the anodic current. However, translating these thermodynamic advantages into practical systems is constrained by electrode consumption and coproduct management. Carbon-based oxidation strategies illustrate extreme cases of voltage minimization but further highlight the trade-offs between energetic gains, material durability, and downstream handling requirements.

The second group comprises coproduction substrates, in which the anode is designed to generate market-relevant chemicals instead of low-value oxygen. In this category, alcohols and polyols are prominent because they can be converted into acids, aldehydes, or other oxygenates. In contrast, primary amines can be converted into nitriles under appropriate catalytic conditions. In this configuration, the hybrid electrolyzer operates as a paired system that produces hydrogen and a second product stream with potential economic value.

The third group comprises remediation-oriented substrates in which the anodic reaction addresses an environmental liability, such as wastewater constituents or pollutants, while still enabling hydrogen generation. In such cases, the product may be treated as effluent or a less harmful chemical form rather than a commodity chemical.

Alcohols and polyols constitute the most extensively explored substrate family for coproduction. Their oxidation networks offer multiple controllable branching points. Under selective reaction pathways, ethanol oxidation can yield acetic acid. Similarly, benzyl alcohol oxidation can produce benzoic acid, while various biomass-derived polyols can be converted into formate, aldehydes, or carboxylic acids, depending on catalyst identity, electrolyte environment, and applied potential. These systems illustrate a broader principle of substrate selection [40]. The best substrate is not necessarily the one with the lowest theoretical anode potential, but rather the one that can deliver a stable, high-FE pathway to a concentrated, separable product slate at the intended current density. This consideration is crucial for polyols and biomass-derived oxygenates, where deep oxidation and C—C cleavage can quickly broaden the product distribution unless the catalyst surface and operating window are tuned to favor a defined subset of intermediates and products.

Aldehydes constitute a distinct region of the anodic reaction space, enabling very-low-voltage operation under selected conditions. When adsorption and electron-transfer steps are well aligned, oxidation can be both thermodynamically favorable and kinetically rapid. In this context, small-molecule aldehyde systems have been reported to approach cell voltages as low as ~0.3 V vs. RHE in specific demonstrations. At the same time, aldehydes are highly reactive and can introduce competing side reactions [41]. To avoid loss of selectivity, volatility issues, or the need for complex downstream separations, their oxidation products may require careful management. As a result, aldehydes are most compelling when they are available

within controlled feedstock streams and when product capture and purification can be integrated into the process design.

Nitrogen-containing substrates occupy another strategically important segment of the anodic reaction space. Urea oxidation is particularly attractive, as it can be integrated with wastewater remediation by converting a prevalent waste constituent into benign products while simultaneously lowering the anode potential relative to OER. Beyond urea, oxidation of amines to nitriles has been discussed as both a chemical upgrading route and, in some contexts, an electro-dehydrogenation strategy relevant to liquid organic hydrogen carriers. For these nitrogen-bearing feeds, substrate selection must explicitly account for safety, toxicity, and membrane compatibility, because volatility, odor, and crossover can impose operational constraints even when electrochemical performance is favorable. Furthermore, nitriles and related products can be valuable, but they require stringent control of selectivity and purification [20].

Biomass- and waste-derived substrates extend hybrid electrolysis beyond a laboratory concept to a circular-economy platform, but they impose stringent selection criteria. Raw sugarcane juice, for example, has been reported to support the coproduction of formic acid and hydrogen, demonstrating that minimally processed agricultural streams can serve as anodic feeds rather than solely purified model compounds [42]. Likewise, lignin-derived molecules and other complex streams are promising feedstock sources that support sustainability narratives. However, these feeds are chemically complex and often contain impurities that can poison catalysts, foul porous electrodes, or accelerate membrane and ionomer degradation [43]. When wastewater or low-quality water is targeted, substrate selection must therefore account for impurity tolerance, resistance to poisoning and fouling, and stable operation under variable composition.

Across these substrate families, selection can be framed as a multi-constraint optimization problem instead of a single-criterion choice. At a minimum, five coupled criteria should be evaluated. First, within the intended electrolyte and concentration range, thermodynamic advantage must be meaningful since real feeds rarely operate under standard conditions. Second, kinetics must remain favorable at the target current density, which requires an intrinsically active catalyst, sufficient substrate mass transport to the anode, and effective removal of products that may inhibit turnover. Third, anodic reaction must maintain high faradaic selectivity against competing OER, particularly as the anode potential increases during high-rate operation. Fourth, alongside separability, product value must be considered since a low-value or diluted product mixture can negate the benefit of voltage reduction. Fifth, feedstock logistics and robustness must be plausible at scale, including availability, cost, safety, storage, and compatibility with membranes and balance-of-plant components.

Whether a substrate is practically viable, two additional considerations need to be determined. One is carbon balance, and the other is the desired oxidation depth. For certain applications, deep oxidation into small molecules is acceptable or preferred. For chemical coproduction, partial-oxidation selectivity is essential and must remain stable over time. Integration strategy is equally critical, as batch, flow-through, and fed-batch configurations impose different concentration profiles and product accumulation behaviors that strongly affect reaction kinetics

and selectivity. Reports emphasizing flow-based operation for alcohol-assisted systems indicate that substrate selection should be aligned with the operating mode that maintains the surface in a selective regime [15].

In summary, in hybrid water electrolysis, the anodic reaction space spans energy-saving, coproduction, and remediation chemistries. Currently, alcohols and polyols, aldehydes, urea, amines, and biomass-derived feeds are among the most prominent substrate classes. Practical selection of an anodic substrate should be driven by an explicit match between thermodynamic and kinetic feasibility at the target current density. In addition, the ability to suppress competing OER while maintaining high selectivity, together with product value and feedstock robustness, ultimately governs scalability.

1.4 Advantages Beyond Voltage: Coproduction, Safety, and Sustainability

The most visible benefit of hybrid water electrolysis is voltage reduction. However, voltage reduction alone is insufficient to reflect the overall value of hybrid water electrolysis. In practice, hybrid systems can offer three additional advantages that are often decisive for deployment. These are the coproduction of value-added chemicals at the anode, improved safety and operational flexibility through suppression of OER, and sustainability gains enabled by coupling hydrogen production with waste conversion and the use of circular feedstocks. In Table 1.2, these advantages

Table 1.2 Summary of advantages beyond voltage and associated practical constraints. Comparative overview of the principal non-voltage benefits of hybrid electrolysis: namely, coproduction of value-added chemicals, improved safety through reduced OER, and sustainability gains via waste and biomass utilization.

Advantage	What you gain	What must be true	If not addressed
Chemical coproduction	Value-added liquids	High FE to target, stable selectivity, feasible separation	Broad mixtures, separation penalty, low net value
Product quality/ separability	Simplified processing	Narrow product slate, minimal crossover, electrolyte pH control	Cross-contamination, neutralization burden, low-purity streams
Safety (gas management)	Reduced O_2 handling	Suppressed OER, separation reliability, low gas crossover	O_2 formation, mixed-gas risk, pressure/venting limits
Durability (materials stability)	Extended lifetime, voltage stability	Corrosion-tolerant, membrane stability, fouling control	Activity drift, membrane decay, performance decay
Sustainability/ waste valorization	Waste removal, H_2 production	Impurity tolerance, pretreatment, stable operation	Poisoning/fouling, feed instability, frequent shutdowns

are summarized. Such factors are interconnected and become practically significant only when selectivity, durability, and separations are engineered alongside electrochemical performance.

1.4.1 Coproduction: Transforming the Anode into a Chemical Manufacturing Module

In conventional water electrolysis, the anode produces oxygen, which is frequently treated as a low-value by-product, particularly in distributed hydrogen production scenarios where oxygen capture, compression, and utilization are not economically attractive. Hybrid electrolysis reframes the role of the anode by enabling the selective generation of targeted chemicals. This shift goes beyond producing a single product stream and fundamentally alters the economics of the electrolyzer, as the anode acts as a chemical conversion module whose outputs can carry significant market value. Alcohols, polyols, aldehydes, and amines are frequently examined as anodic substrates, as their oxidation pathways can yield commodity or specialty oxygenates, acids, or nitriles.

When the anodic product slate is narrow, stable over time, and sufficiently concentrated for economical separation, coproduction advantage is strongest. In selective oxidation systems, small changes in potential, local pH, or surface coverage can shift reaction pathways, meaning that high instantaneous FE alone is insufficient if product distributions drift during continuous operation. For practical deployment, performance must approach that of electrosynthesis, with stable selectivity and carbon balance maintained at relevant current densities and timescales. When these criteria are met, hybrid electrolysis can operate as a paired process that produces hydrogen while upgrading low-value feedstocks into higher-value chemicals.

Coproduction also permits application-specific optimization. The most suitable anodic reaction depends on local feedstock availability and the product value chain. In regions with abundant bio-derived polyols or agricultural streams, oxidation pathways that yield organic acids or formate may be attractive. In chemical manufacturing contexts, selective oxidation to aldehydes, ketones, or nitriles may be prioritized. Hybrid electrolysis can thus complement conventional electrolyzers rather than compete directly with them. In applications where oxygen is valuable and oxygen-handling infrastructure is available, OER-based systems remain compelling. For settings where oxygen is a burden, hybrid coproduction becomes more attractive.

1.4.2 Safety and Operational Flexibility: Reducing Oxygen-related Constraints

Safety considerations are integral to electrolyzer design. The concurrent generation of hydrogen and oxygen poses inherent risks associated with gas crossover and mixing, particularly in compact systems where membrane crossover, sealing failures, or off-nominal operating conditions can lead to hazardous compositions. By suppressing OER under operating regimes in which organic oxidation predominates, hybrid

electrolysis offers an intrinsic safety lever. Reduced or eliminated oxygen production mitigates hazards related to H_2/O_2 coexistence, simplifies gas-handling requirements, and alleviates demands on oxygen-separation and venting infrastructure.

The practical impact of this safety advantage depends strongly on the anodic chemistry. In many alcohol-assisted systems, the anodic product stream is primarily liquid-phase and generates minimal gaseous oxygen when OER is effectively suppressed. In other hybrid chemistries, gaseous products such as CO_2 or N_2 may be produced, depending on the substrate and pathway. These gases can be less reactive than oxygen with respect to hydrogen safety, but still require appropriate venting and management. The safety benefit should therefore be stated precisely. Hybrid electrolysis can reduce OER and thus oxygen-specific hazards, but it does not eliminate the need for gas-management strategies.

Hybrid electrolysis can provide operational flexibility. When anodic kinetics are more favorable than OER, lower cell voltages at a given current density may be achieved, expanding the operating envelope under fluctuating renewable power inputs. However, this flexibility is conditional. Depletion of the anodic substrate, catalyst poisoning, or mass-transport limitations can increase anode potential and promote the reemergence of OER, diminishing both voltage and safety advantages. Sustained operation requires maintaining the anode in a regime where the intended oxidation reaction remains dominant. This requirement depends on catalyst selection, electrode architecture, and operating strategy, often favoring continuous-flow or fed-batch configurations.

1.4.3 Sustainability and Circularity: Coupling Hydrogen with Waste Conversion

For hybrid electrolysis, the sustainability argument is most compelling. It enables coupling renewable electricity with the conversion of waste streams into hydrogen and other valuable products or benign effluents. Urea-containing wastewater is a frequently discussed case. In domestic and agricultural contexts, it is abundant and can serve as a low-potential anodic reaction while contributing to nitrogen waste mitigation. Within this framework, hybrid electrolysis functions as a combined energy and environmental technology that produces hydrogen while addressing wastewater treatment needs.

More generally, biomass-derived substrates, including lignin-derived aromatics, agricultural juices, and polyol-rich streams, allow hybrid electrolysis to be integrated into biorefineries and agro-industrial value chains. The use of sugarcane juice as an anodic feed for formic acid and hydrogen coproduction demonstrates that minimally processed streams can be used instead of purified model compounds. When coupled with biomass upgrading, hybrid electrolysis supports circular carbon use by partially converting organic streams into valuable oxygenates while simultaneously producing hydrogen. This approach is particularly attractive for distributed systems in regions with abundant biomass resources and growing renewable electricity capacity.

Sustainability benefits must be assessed realistically, especially for waste-derived feeds. Such feeds are chemically complex and can contain impurities that cause

catalyst poisoning, membrane and ionomer degradation, and electrode fouling, increasing maintenance needs and reducing component lifetimes. To achieve genuine environmental benefits, hybrid electrolysis systems must use impurity-tolerant catalysts and materials, apply minimal but effective pretreatment, and avoid shifting environmental burdens elsewhere in the process.

1.4.4 Interdependence of Advantages and the Role of System-level Metrics

Coproduction, safety, and sustainability are not independent attributes. Coproduction is meaningful only if selectivity is maintained and products can be recovered at acceptable energy and cost. Moreover, safety benefits associated with oxygen suppression are realized only when operating conditions maintain OER suppression under realistic operation, including transient events and long-term degradation. Sustainability benefits derived from waste conversion depend on tolerance to real feeds and on a favorable overall environmental balance once separations, pretreatment, and component replacement are taken into account.

This interdependence implies that hybrid electrolysis should be evaluated using system-level metrics rather than isolated half-cell performance indicators. In addition to cell voltage and hydrogen FE, key metrics include product-resolved FE, carbon balance closure, stability of product distribution, and energy consumption per unit of hydrogen and per unit of target chemical. Where remediation is a primary goal, metrics such as removal efficiency and effluent quality are also essential. These measurements provide a quantitative basis for assessing whether the broader advantages of hybrid electrolysis translate into practical impact and for identifying configurations that merit further development and scale-up.

In summary, hybrid water electrolysis offers advantages that extend well beyond voltage reduction. By enabling the coproduction of value-added chemicals, it can improve process economics and create new opportunities for integration with chemical and biomass value chains. By suppressing OER under relevant operating regimes, it can mitigate oxygen-related hazards and simplify gas-handling requirements, provided that OER suppression is maintained under realistic and long-term conditions. By utilizing waste-derived or biomass-derived substrates, hybrid electrolysis can couple hydrogen production with environmental remediation and circular resource utilization. Realizing these advantages at scale will require precise control over selectivity and stability, ensuring compatibility with membranes and balance-of-plant components, and the development of operating modes and separation strategies that translate electrochemical performance into robust, deployable systems.

1.5 Remaining Challenges and Outlook

Hybrid water electrolysis is attractive. It can reduce electrical energy input by replacing OER with an alternative AOR. This approach enables chemical coproduction and, in some cases, the valorization of wastewater or biomass-derived substrates.

However, the use of complex anodic chemistries introduces practical challenges. These challenges extend beyond achieving low voltage and high current in short-term tests. Instead, they relate to maintaining selectivity, durability, and economic viability under realistic feed conditions, device designs, and long-term operation.

In hybrid water electrolysis, a primary bottleneck is product selectivity and faradaic partitioning at the anode. Organic oxidation reactions proceed through multiple surface-bound intermediates, and their pathways depend on the applied potential, local pH, substrate concentration, and changes in the catalyst surface. As a result, a catalyst can sustain high anodic currents while producing an undesired or unstable product distribution, thereby undermining the rationale for coproduction and complicating downstream separation. Selectivity should therefore be considered a time-dependent property rather than a single-point metric. As the catalyst reconstructs and active sites become blocked, or the local reaction environment within porous electrodes evolves, product distributions can change. These effects are more severe at industrially relevant current densities, where concentration gradients, mass-transport limitations, and shifts in anode potential promote deeper oxidation and side reactions.

Closely related to the challenge of maintaining selectivity is competition from residual OER at the anode. Even when an alternative AOR is thermodynamically favored, OER can reappear if the desired organic pathway is impeded by substrate depletion, catalyst poisoning, or mass-transport limitations. This competition leads to a dual penalty: part of the current is diverted to OER, reducing the voltage advantage, while the charge contributing to target products decreases, lowering FE and product yield. Suppressing OER is both a catalytic challenge and a challenge in reactor design, requiring a stable substrate supply and effective removal of inhibitory products to keep the anode potential out of the OER-dominated regime.

Catalyst robustness under realistic operating conditions represents a second major challenge for hybrid water electrolysis. Hybrid water electrolysis exposes the anode catalyst to coupled electrochemical and chemical stresses. Reactive organic intermediates, strongly oxidizing potentials during transients, local pH shifts, and continuous adsorption–desorption cycles can restructure the surface. Even when the bulk phase is nominally stable, the catalytically active surface often evolves into oxygenated or hydroxylated states. This evolution is beneficial only if it remains controlled and electronically connected. Uncontrolled reconstruction can reduce active-site density, alter adsorption energetics in ways that degrade selectivity, or accelerate dissolution and detachment from supports. Durability must be evaluated in terms of both activity and selectivity. Retention of both is essential, because a stable current density can otherwise be sustained by a gradual shift toward less selective pathways or increased OER contributions.

System design constraints constitute a third barrier that often determines whether promising catalysts can be translated into practical devices. Membranes and ionomers play a critical role in many electrolyzer configurations, particularly when product separation and gas management are required. However, organic feedstocks introduce additional compatibility challenges, including swelling, chemical

degradation, and changes in ionic conductivity. Crossover of organic substrates and products can reduce coulombic efficiency, contaminate the cathode, and complicate downstream processing. At the same time, membranes can provide important benefits by enabling compartmentalization, stabilizing selectivity, and supporting continuous operation, provided that crossover is effectively controlled. The associated engineering challenge is therefore a trade-off: transport of the desired ionic species must be maximized, while transport of neutral organics and reactive products should be minimized.

A fourth major challenge concerns separations and process intensification. When the anode produces a usable chemical stream, hybrid water electrolysis offers clear value. However, electrosynthetic product concentrations are often low, and product mixtures can be complex. If product recovery requires energy-intensive separations, the system-level benefit may be diminished even at low electrolyzer voltages. Substrate selection, catalyst selectivity, and reactor configuration must therefore be evaluated in an integrated manner. Flow operation can increase effective product concentration and limit over-oxidation by controlling residence time. In contrast, batch operation may lead to progressive product degradation or secondary reactions as electrolysis proceeds. In system-level design, the anode should be treated as an integrated conversion and pre-separation unit rather than merely as an oxygen-evolving electrode.

Feedstock realism is a fifth and increasingly important barrier. Many hybrid systems are demonstrated using purified model compounds, but scale-relevant deployment is likely to involve complex feeds such as biomass-derived streams, industrial effluents, or wastewater constituents. These feeds contain inorganic ions and diverse organics that can poison catalysts, foul porous electrodes, and degrade membranes. Addressing this gap requires catalysts with impurity tolerance, electrode architectures that resist fouling while maintaining mass transport, and pretreatment strategies that are minimal but effective. The appeal of using waste-derived substrates and even waste-derived catalysts as a route toward circular green hydrogen has been emphasized. Still, it also poses challenges for long-term stability and reproducibility under variable feed compositions.

Benchmarking and reporting practices constitute a sixth challenge that shapes the field's evolution. Because hybrid electrolysis simultaneously targets hydrogen production and selective oxidation, performance claims must account for both aspects of the system. Meaningful benchmarking requires, at a minimum, cell voltage at specified current densities, hydrogen FE, product-resolved FE, carbon balance closure, and stability over time under controlled operating conditions. When suppression of OER is claimed, quantifying O_2 evolution or demonstrating its absence within the detection limit is necessary. Without consistent reporting, comparisons across catalyst families and substrates remain ambiguous, and conclusions about deployment potential can be fragile.

In summary, the remaining challenges for hybrid water electrolysis center on selectivity control and suppression of competing OER, catalyst and component durability, membrane and crossover management, separations feasibility, and validation under realistic feeds and operating conditions. The chapter sequence

is designed to address these issues systematically: first by establishing shared performance metrics, second by mapping catalyst families to substrate classes, and finally by connecting material advances to engineering and deployment constraints.

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