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Recent advances in interfaces and durability of electrochemical cells and electrocatalytic systems

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Systematic Review

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Recent advances in interfaces and durability of electrochemical cells and electrocatalytic systems

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Abstract

Batteries, fuel cells, electrolyzers and electrocatalytic reactors are usually discussed separately, yet they tend to fail at the same kind of place: an interface. This review draws on 102 open-access articles published between 2019 and 2026, follows that thread across cells and catalysts, and collects the quantitative findings reported in them. Inorganic solid electrolytes span conductivities of 10^{-5} to 10^{-2} S cm^{-1} depending on class, and the sulfides that reach the highest values are prone to interface and moisture problems. Electrolyzers run at 40–90 °C in liquid-alkaline, anion-exchange and proton-exchange cells and at 600–850 °C in solid-oxide cells. For oxygen evolution in alkaline media, a nickel–iron oxyhydroxide needs overpotentials of 251 and 291 mV at 100 and 500 mA cm^{-2} and runs for more than 300 h, and a cobalt–ferrocene framework needs about 190 mV at 10 mA cm^{-2}; both are formed by reconstruction of a precatalyst during operation. Single-atom catalysts approach 100 % atom utilization, yet the longest laboratory stability test quoted here, over 300 h, is under 0.4 % of the 80,000 h lifetime targeted for PEM electrolyzers. In CO_2 electrolyzers, current densities above 200 mA cm^{-2} are reached, but salt precipitation limits operation. We compare six catalyst families together with operando characterization and machine learning, and conclude that standardized reporting, device-relevant testing and assignment of activity to the working state now matter more than new compositions.

Keywords: electrocatalysis; solid-state batteries; water electrolysis; CO_2 reduction; operando characterization; machine learning

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1. Introduction

Most readers meet electrochemistry through one device at a time. A battery paper talks about ions moving through bulk phases and about the films that form on electrodes. A catalysis paper talks about adsorbed intermediates, scaling relations and turnover. The vocabulary differs, but the underlying problem is shared: charge has to cross a boundary between two phases, and the boundary rarely stays the way it was made.

The overlap is easy to see in recent reviews. Work on solid-state lithium batteries returns again and again to the contact between solid electrolyte and electrode rather than to the bulk conductivity of the electrolyte itself [1–3]. Work on water electrolysis and fuel cells, in turn, increasingly asks how catalysts, ionomers and membranes behave together, not just how active a catalyst looks in a three-electrode cell [4–6]. The same pattern appears in CO_2 electrolysis, where recent studies concentrate on salt precipitation in the cell and on the local environment around the catalyst [7–9].

Three developments stand out. The first is a shift in catalyst design toward atomically defined and compositionally complex materials. Single-atom catalysts are now reviewed for reactions that range from water splitting to ammonia production [10], and dual-atom designs have been surveyed from theory to application [11]. High-entropy materials, in which five or more elements share one lattice, form a separate and fast-growing branch [12–14].

The second change is a move from the catalyst to the whole reaction environment. Reviews of acidic CO_2 electroreduction now treat the electrolyte, the local microenvironment and the

electrode structure as design variables alongside the catalyst [9], and dedicated reviews exist for copper catalysts working inside a membrane electrode assembly [15].

The third is the arrival of new reactions and new tools. Nitrate reduction to ammonia has attracted a large number of reviews in the past two years, since it can pair ammonia synthesis with removal of a pollutant [16–19]. Machine learning, meanwhile, has moved from proof-of-concept studies to a routine part of catalyst design [20–23]. A fourth, quieter development is that batteries themselves now depend on catalysis: lithium–sulfur cells use electrocatalysts against the polysulfide shuttle [24], and zinc–air cells live or die by their bifunctional oxygen catalysts [25, 26].

Work on energy storage shows how much of a cell's performance is decided away from the bulk of its materials. Inorganic solid electrolytes are grouped into oxides, sulfides and halides, whose room-temperature conductivities are reported as 10^{-5} to 10^{-3}, 10^{-3} to 10^{-2} and 10^{-4} to 10^{-2} S cm^{-1}, respectively [27]. The sulfides, which sit at the top of that range, are also the class that reacts with electrodes and with moisture, so resistive interphases and handling constraints follow the conductivity [28, 29]. On the cathode side, layered oxides with at least 80 % nickel are favoured for capacity, but reviews describe surface degradation, cation mixing, microcracks and gas release at high voltage [30, 31]. Metal–air and metal–sulfur cells move the problem into catalysis: zinc–air batteries are reviewed with reported energy densities of up to 1086 Wh kg^{-1} [32], but only if the air cathode catalyses both oxygen reduction and oxygen evolution at low overpotential [25, 26], and lithium–sulfur cells need electrocatalysts to deal with the polysulfide shuttle [24].

In electrolysis and fuel cells the same theme appears, now with numbers attached to the operating regime. A materials review lists operating temperatures of 60–90 °C for liquid

alkaline, 40–70 °C for anion-exchange-membrane, 50–80 °C for proton-exchange-membrane and 600–850 °C for solid-oxide electrolyzers [33]. Anion-exchange-membrane electrolysis is positioned between alkaline electrolysis, which is limited in productivity and efficiency, and PEM electrolysis, which relies on critical raw materials [4]. The catalyst layer is a design variable in its own right: ionomer thin-film electrodes are reported to have reduced the platinum loading of PEM fuel cells to 0.4 mg cm^{-2} [34]. At the level of a single reaction, oxygen evolution gives a useful benchmark. A nickel–iron oxyhydroxide that combines adsorbate-evolution and lattice-oxygen pathways needs overpotentials of 251 ± 5 and 291 ± 1 mV at 100 and 500 mA cm^{-2} in alkaline media and stays stable for more than 300 h, and it is formed by reconstruction of a $NiMoO_4$ precatalyst during operation [35]. Seawater adds a chemical constraint, because it contains about 0.5 M chloride, which lets chlorine evolution compete with oxygen evolution [36]. For CO_2, copper remains the only metal reported to make multicarbon products in aqueous electrolyte [37].

Catalyst design, characterization and computation then try to turn these observations into rules. Single-atom catalysts are valued for atom utilization of almost 100 % and for coordination environments that can be tuned, for example through asymmetric low-coordination, heteroatom and dual-metal sites in CO_2 reduction [38, 39]. High-entropy materials add many-element sites and have been reviewed for hydrogen evolution, oxygen evolution, oxygen reduction and CO_2 reduction [13, 14]. Because reconstruction can change the active phase, as in the nickel–iron case above and in a cobalt–ferrocene framework [40], operando X-ray absorption and vibrational spectroscopy have become routine tools [41, 42], and machine learning is now used to screen candidates and extract trends [20, 21]. The device literature supplies the hardest test. In zero-gap CO_2 electrolyzers, salt precipitation limits operation and has to be mitigated through operating

strategy and cell design [7, 8], and in PEM water electrolyzers, accelerated stress tests identify platinum dissolution and iridium oxidation as key degradation routes [43]. Taken together, these data describe a field in which half-cell activity looks increasingly impressive, while the data that decide durability in devices remain sparse and hard to compare, which is the gap this review addresses [44, 45].

Existing reviews are valuable but are usually organized around one reaction, one material class or one technique, and each is strong on its own topic and silent on the neighbouring ones. Reviews of solid-state batteries concentrate on solid electrolytes and anodes [1, 2, 27]. Reviews of electrocatalysts are organized by catalyst type, for example single-atom [10] or high-entropy materials [12–14], or by reaction, for example acidic CO_2 reduction [9, 15] or nitrate reduction to ammonia [16–19]. Characterization and computation have their own reviews, on in situ and operando methods [41, 46] and on machine learning [20–22]. A smaller set of papers sits between batteries and catalysis, covering electrocatalysts in lithium–sulfur and zinc–air cells [24–26, 32, 47].

What is missing is a treatment that connects these strands. The questions that now decide progress, namely how interfaces change during operation, how to separate intrinsic activity from reconstruction, and why a catalyst that performs well in a half-cell can struggle in a device, cross all of the topics above. This review tries to connect them.

We pursue four aims. First, to compare the main electrochemical cells by architecture and failure mode. Second, to summarize the principles behind activity and selectivity. Third, to assess recent catalyst families together with the operando and computational tools used to judge them. Fourth, to examine the gap between half-cell results and working devices.

2. Electrochemical Cells: Architectures and Failure Modes

2.1 One skeleton, many devices

Every cell in this review follows the layout in Figure 1: two electrodes, an ion-conducting medium between them, and an external circuit for the electrons. Run spontaneously, the cell is a battery or fuel cell. Driven by an applied voltage, it is an electrolyzer or a charging battery. The voltage a working cell actually delivers differs from the thermodynamic value by three losses, namely ohmic, kinetic and mass-transport losses, and almost every strategy discussed below can be read as an attempt to shrink one of them. We keep returning to Figure 1 because the middle block, the electrolyte or membrane, is where the devices differ most, and where most of their failure modes originate.

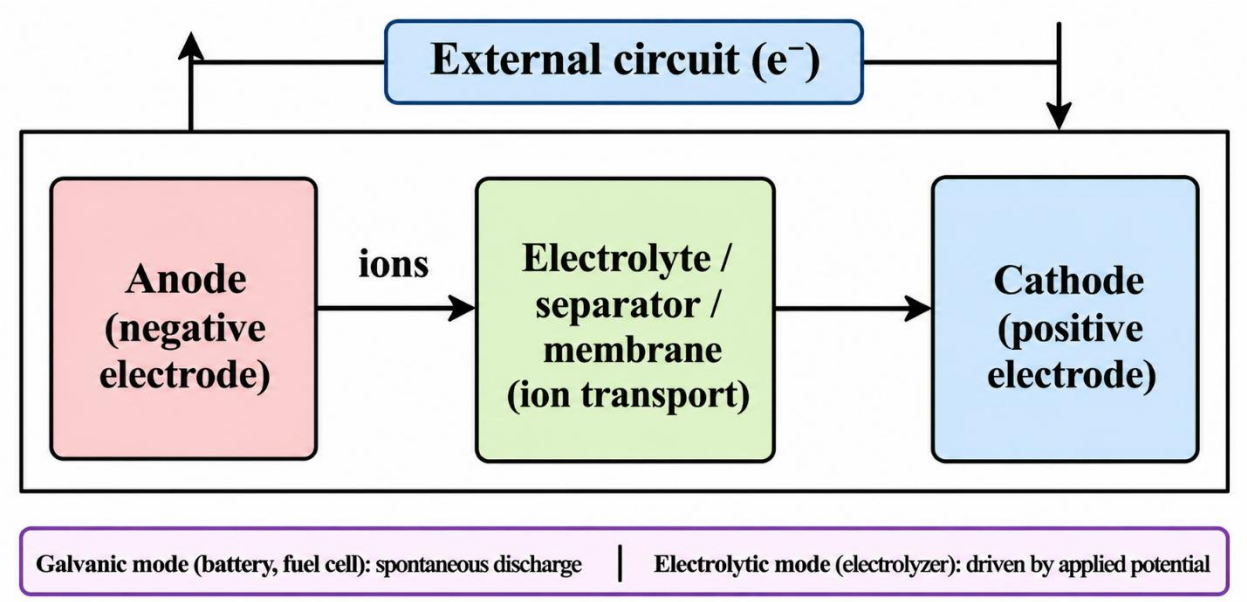

Figure 1. Generic electrochemical cell. Ions cross the electrolyte or membrane while electrons travel through the external circuit. The same layout covers galvanic devices (batteries, fuel cells) and electrolytic devices (electrolyzers) (original schematic prepared for this review).

2.2 Liquid-electrolyte lithium-ion cells: cathodes and safety

Liquid-electrolyte lithium-ion batteries remain the reference technology, and two issues recur in the literature: the stability of high-capacity cathodes and the safety of the electrolyte. On the cathode side, nickel-rich layered oxides are leading candidates for high capacity, yet reviews describe a consistent set of problems at high voltage: surface degradation and a resistive surface film, cation mixing that turns the layered phase into spinel or rock salt, gas release and microcracks [31, 48]. The remedies are reviewed as well, namely element doping, surface coating, single-crystal fabrication, concentration gradients, structural design and electrolyte additives [31, 48], and surface modification by coating, surface doping and washing has been compared for its advantages and shortcomings [30]. Table 1 lines up each problem with the reported strategies.

Table 1. Reported problems of nickel-rich layered cathodes and the strategies that reviews propose.

Problem	Reported description	Strategy	Reference
Surface degradation	Side reactions with electrolyte; high-resistance surface film	Surface coating; electrolyte additives	[30, 31]
Phase change	Cation mixing; layered to spinel or rock salt	Element doping; structural design	[31, 48]
Microcracks	Contact failure and repeated surface reactions	Single-crystal fabrication; concentration gradients	[31, 48]
Gas release	Gas evolution at high operating voltage	Surface modification	[31]
Transition-metal	Loss of active material at high	Doping; coating; particle	[48]

Problem	Reported description	Strategy	Reference
dissolution	voltage	engineering	

On the electrolyte side, thermal runaway develops from the interaction of materials and cell design [49], and a recent review follows failure modes from materials up to systems [50]. One response is to make the liquid itself safer, and nonflammable liquid electrolytes are an active research line [51]. Another is to remove the liquid altogether, which leads to the solid-state cells in the next section.

2.3 Solid-state lithium batteries

The reviews we examined agree on how solid electrolytes should be grouped: inorganic ceramics (oxides, sulfides and halides), polymers, and composites of the two [1, 27]. What they also agree on, perhaps more importantly, is that each class carries a trade-off. Table 2 summarizes the comparison as reported in one recent review [27]. Oxides are chemically and thermally robust but make poor physical contact with electrodes. Sulfides conduct best and deform easily, but are unstable against many electrodes and sensitive to moisture. Halides tolerate high voltages but are chemically less stable. None of the classes wins on every row, which is why composites have become so popular [52]. A recent review makes the same point from an engineering angle: it compares oxide, sulfide, halide, nitride, polymer and composite electrolytes by transport, chemical stability, mechanical response, interface evolution and processability, and stresses low stack pressure and scalable manufacturing as conditions for practical cells [53].

Table 2. Main classes of inorganic solid electrolytes. Conductivity ranges and qualitative strengths and weaknesses are those reported in the cited review; the ranges are indicative and depend on composition and processing.

Class	Conductivity at 25 °C (S cm^{-1})	Strengths	Weaknesses	Reference
Oxide	10^{-5} to 10^{-3}	High chemical and thermal stability; good mechanical strength	Poor contact with electrodes; costly production	[27]
Sulfide	10^{-3} to 10^{-2}	High conductivity; good interfacial adaptability	Low chemical stability; sensitive to moisture; narrow electrochemical window	[27, 29]
Halide	10^{-4} to 10^{-2}	Good deformability; high oxidation voltage	Low chemical stability; moisture sensitivity; unstable against lithium metal	[27]

Sulfides deserve a closer look because they combine the highest conductivities with pronounced interface and moisture problems. Reviews describe how their instability in contact with electrodes produces resistive interphases that degrade cell performance [28], and how composite cathodes and the cathode–electrolyte interface remain the main obstacle to commercialization [29, 54]. Moisture and air sensitivity add a processing burden on top of this [29].

On the anode side, lithium metal is the prize and the problem. Dendrite growth and an unstable solid–electrolyte interphase affect both liquid and solid systems [55, 56], and solid electrolytes

help only if they stay in contact with the metal during cycling [2, 3]. Interlayers, coatings and nanocomposite microstructures are therefore discussed as often as new electrolyte compositions [1, 52]. A word of caution applies to all of this literature: interface studies at the nanoscale show how complicated the real situation is [57], and laboratory cells with small areas and excess lithium do not necessarily predict how a large cell will behave. Machine-learning models have started to help with electrolyte screening [58], a point we return to in Section 7.

2.4 Where batteries need catalysts: lithium–sulfur and zinc–air cells

Two battery types make the link between the cell and catalysis sections of this review explicit. In lithium–sulfur cells, the shuttle of soluble polysulfides is the central problem, and MXene-based electrocatalysts are reviewed with emphasis on structure–activity relationships under high sulfur loading and lean electrolyte [24]. In zinc–air cells the air cathode has to catalyse oxygen reduction on discharge and oxygen evolution on charge, so the cell is only as good as its bifunctional catalyst. Reviews cover transition-metal-based catalysts as replacements for precious metals [32], catalysts grouped as platinum-group, metal-free, transition-metal and framework-derived [25], design principles [26] and comparisons of battery performance [47]. Table 3 lists the classes. Because the oxygen reactions in a zinc–air cathode are the same ORR and OER discussed in Sections 4.2 and 4.3, the catalyst families of Section 5 apply here directly.

Table 3. Catalyst classes for the air cathode of rechargeable zinc–air batteries, as grouped in recent reviews.

Catalyst class	Role at the air cathode	Reference
Transition-metal-based	Lower-cost alternative to precious metals for ORR and OER	[32, 47]
Platinum-group metals	Reference activity for oxygen reactions	[25]

Catalyst class	Role at the air cathode	Reference
Metal-free (carbon-based)	Avoids metals; heteroatom-doped carbons	[25, 59]
Framework-derived	Tunable porosity and active sites	[25, 26]

2.5 Sodium-ion and aqueous zinc batteries

Sodium-ion batteries have moved forward mostly through the anode. Hard carbon is the leading candidate, and reviews describe both its sodium-storage mechanisms and the optimization strategies that improve it [60, 61]. Aqueous zinc batteries take a different route to safety. Recent reviews cover layered two-dimensional materials that act as protective layers, hosts and additives [62], organic electrode materials with tunable structures [63], and zinc anodes for zinc–air cells [64]. In both families the practical questions are the same ones we met for lithium: how stable is the interface, and what does it cost to keep it stable?

2.6 Redox flow batteries

Flow batteries separate power from energy by storing the active species in tanks, which suits long-duration storage. Recent reviews compare organic and inorganic chemistries and the reaction mechanisms at the electrodes [65]. For vanadium systems the membrane is the weak point. Work on optimized membranes aims to reduce crossover and cost [66], and systematic ex situ tests of commercial polymer membranes show how widely their properties differ [67].

2.7 Fuel cells and electrolyzers

Proton-exchange-membrane (PEM) devices work in acid and depend on platinum-group metals. Alkaline water electrolysis is cheaper in materials but has been limited in productivity and efficiency, and anion-exchange-membrane (AEM) electrolyzers try to combine the advantages of both [4, 6]. Recent reviews of AEM electrolysis emphasize membrane ion conductivity and

alkaline stability, and the interplay between catalyst, membrane and operating conditions [5, 6]. For PEM electrolyzers, a broad materials review covers every cell component and singles out operation at low iridium loading, membrane durability, multiscale transport layers and flow fields as the key issues [33], and a stack-level review summarizes working principle, components, production technology and cost-reduction strategies [68]. Table 4 puts the main cell types side by side.

Table 4. Qualitative comparison of principal electrochemical cell types, linked to the sections where each is discussed.

Cell type	Ion carrier	Main advantage	Main limitation	Reference	Section
Li-ion (liquid)	Li^+ in organic solvent	Mature technology	Flammable electrolyte; thermal runaway; Ni-rich cathode degradation	[31, 49–51]	2.2
Solid-state Li	Li^+ in oxide, sulfide, halide or polymer	Safety; lithium-metal compatibility	Solid–solid interface; processing	[1, 2]	2.3
Li–S	Li^+; soluble polysulfides	High theoretical energy density	Polysulfide shuttle; needs electrocatalyst	[24]	2.4
Zinc–air	Zn^{2+}/OH^-; air cathode	Abundant zinc; open cathode	Sluggish bifunctional oxygen catalysis	[25, 26]	2.4

Cell type	Ion carrier	Main advantage	Main limitation	Reference	Section
Na-ion	Na^+	Hard-carbon anodes under active development	Anode optimization still needed	[60, 61]	2.5
Aqueous zinc	Zn^{2+} in aqueous electrolyte	Safer aqueous operation	Anode and cathode stability	[62, 63]	2.5
Redox flow	Dissolved redox couples; membrane	Power and energy decoupled	Membrane crossover and cost	[65, 66]	2.6
PEM electrolyzer or fuel cell	H^+ in polymer membrane	Avoids the productivity and efficiency limits of conventional alkaline electrolysis	Critical raw materials; platinum-group metals	[4, 6]	2.7
AEM / alkaline electrolyzer	OH^-	Non-precious catalysts possible	Membrane conductivity and alkaline stability	[4–6]	2.7

Read together, Table 4 and Table 2 show a consistent pattern. The most promising option in each row of the cell table has a limitation that sits at an interface or a membrane, and the solid-electrolyte table shows the same thing at the material level. Both low-temperature electrolyzers and fuel cells are built in the layered form shown in Figure 2, with a catalyst layer on each side

of a membrane and porous transport layers outside. That stack is where many of the durability issues in Section 8 originate.

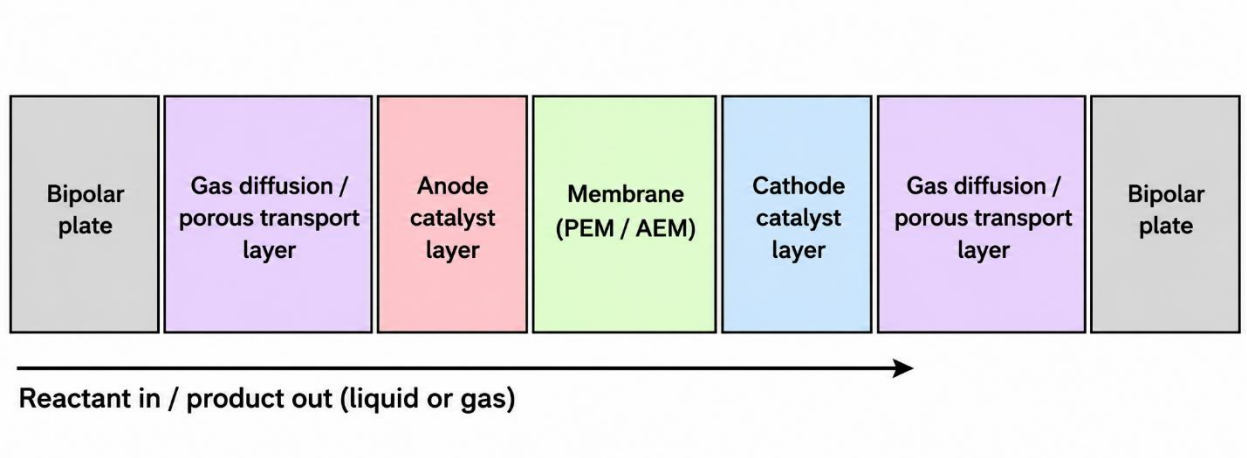

Figure 2. Layered membrane electrode assembly (MEA) used in electrolyzers and fuel cells: bipolar plates, porous transport layers, catalyst layers and a central membrane (original schematic prepared for this review).

3. Fundamentals of Electrocatalysis

3.1 Binding energies and the volcano

A catalyst lowers the barrier of an electrode reaction by offering a different pathway. For many reactions, how well a surface works depends on how strongly it binds one or two key intermediates. If the binding is too weak the reactant is never activated; if it is too strong the product will not leave. The Sabatier principle says that the best surface sits between these extremes, and plotting activity against a binding-energy descriptor gives the volcano shape shown in Figure 3. We include the figure as a reading aid, not as data: the peak marks the best compromise, and the two slopes mark the two ways a catalyst can fail. Many of the catalyst strategies in Section 5 are attempts to move a material toward the top of that curve.

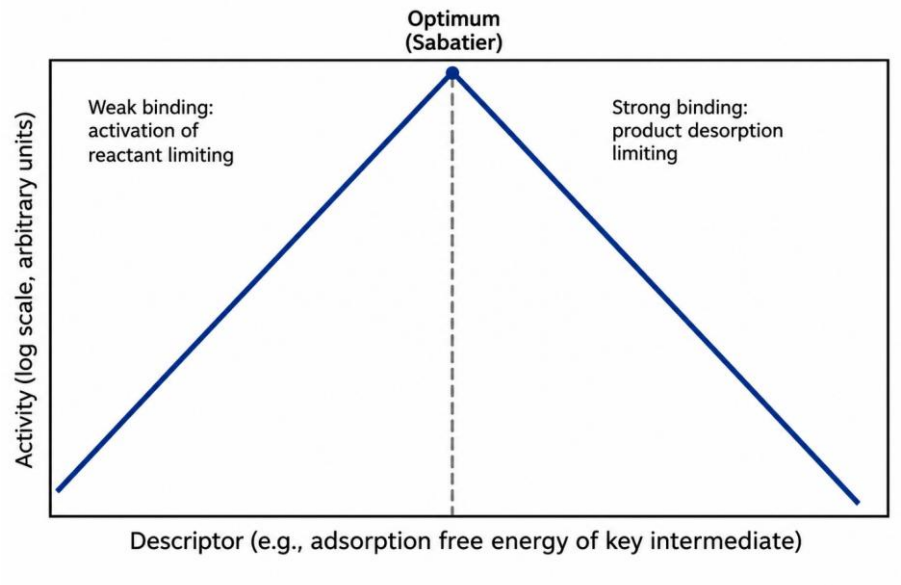

Figure 3. Conceptual volcano relationship between a binding-energy descriptor and catalytic activity. The figure is a schematic and contains no experimental data (original schematic prepared for this review).

3.2 Scaling relations

For multi-step reactions such as oxygen evolution, oxygen reduction and CO_2 reduction, the binding energies of different intermediates on the same surface tend to move together. This linear scaling sets a floor under the overpotential of simple surfaces. A good deal of recent work, including the dual-atom designs reviewed by Pedersen and co-workers [11] and the lattice-oxygen strategies discussed in Section 4.2, can be read as an attempt to get around this floor by giving two intermediates two different kinds of site.

3.3 The reaction environment

Activity is not set by the surface alone. The electrolyte, the local concentration of reactants and the structure of the electrode all change what a given catalyst can do. This is the central message of recent work on acidic CO_2 electroreduction, which treats electrolyte regulation, the local environment and the electrode structure as design variables on equal footing with the catalyst [9].

A direct consequence is that a catalyst ranked first in one electrolyte or cell format may rank lower in another, so comparisons across papers need care.

3.4 Mass transport and gas-diffusion electrodes

Gas-consuming reactions are limited in plain aqueous cells by how slowly the gas reaches the surface. Gas-diffusion electrodes, in which a porous layer brings gas close to the catalyst, remove much of that limit, but they shift the problem to water and ion management inside the electrode. Reviews of membrane electrode assemblies for CO_2 reduction treat these components as part of the catalyst system rather than as background hardware [15], and the same logic holds for oxygen transport in the catalyst layers of fuel cells and water electrolyzers, where bulk and local transport mechanisms and ionomer design determine how much of the catalyst can be used [69]. We return to this in Section 8.

3.5 Metrics, and why they cannot be compared casually

Overpotential at a chosen current density, Tafel slope, turnover frequency, Faradaic efficiency and stability test duration each describe a different aspect of performance. Papers on turnover frequency show how easily these numbers mislead when the number of active sites is unknown or when current is normalized in different ways [45]. For CO_2 electrolysis, a set of best-practice recommendations asks for clear reporting of product quantification, cell conditions and normalization [44]. Table 5 lists the common metrics, what each tells us, and where each one tends to go wrong.

Table 5. Commonly reported electrocatalysis metrics and typical pitfalls.

Metric	What it indicates	Common pitfall	Reference
Overpotential at fixed current density	Energy cost at one operating point	Normalization choice (geometric or surface area) can change rankings	[44, 45]

Metric	What it indicates	Common pitfall	Reference
Tafel slope	Hint about the rate-determining step	Over-reading when mass transport or ohmic drop contributes	[45]
Turnover frequency	Activity per active site	Site counting is uncertain	[45]
Faradaic efficiency	Selectivity to a product	Incomplete product quantification	[44]
Stability duration	Durability	Short half-cell tests do not predict device lifetime	[44, 70]
Mass or specific activity	Cost-relevant activity	Depends on loading and electrode structure	[45]

The practical lesson of Table 5 is straightforward: whenever a paper reports only one or two of these metrics, the reader should ask what the missing ones would show. We apply the same standard to the comparisons in the rest of this review.

4. Key Electrocatalytic Reactions

4.1 Hydrogen evolution reaction (HER)

The hydrogen evolution reaction is the cathode half-reaction of water electrolysis and the simplest of the reactions we cover. Platinum is still the benchmark, and a large part of the literature asks how far abundant elements can go. Transition-metal phosphides, for example, have been studied intensively as HER catalysts in alkaline media, with reviews examining their structure, activity and the strategies used to improve them [71]. Frameworks are a more recent route: covalent organic frameworks have been proposed as water-splitting electrocatalysts, offering designable porosity and molecular-level control of the active site [72]. Interfaces matter here as well; nanoscale hetero-interfaces are reviewed for both electro- and photocatalytic water

splitting [73]. Carbon-based materials are a further option: carbon nanohorns, for example, have been surveyed as electrocatalysts for oxygen reduction, hydrogen evolution and oxygen evolution [59].

Industrial operation raises the bar. At ampere-level current densities, the challenges grouped by a recent review are catalytic activity, mass diffusion (including bubble detachment) and catalyst stability [74]. Direct seawater adds a chemical problem on top: chloride competes through the chlorine evolution reaction and corrodes electrodes, so selectivity and corrosion resistance become design targets next to activity [36, 75].

4.2 Oxygen evolution reaction (OER)

The oxygen evolution reaction is the efficiency bottleneck of water electrolysis, because four proton–electron transfers and an O–O bond must come together. In acid, iridium- and ruthenium-based oxides are the reference materials, and reviews cover the mechanisms, optimization strategies and remaining challenges for Ru- and Ir-based catalysts [76], for RuO_2 in particular [77], and for mixed-metal oxides [78, 79]. Stability in acid is the real constraint, and a recent review of platinum-group-metal OER catalysts argues that test parameters and protocols need to be standardized if durability is to be compared at all [70]. In alkaline media the picture is different: design strategies and structure–activity relationships have been reviewed for catalysts that rely on abundant elements [80]. Layered double hydroxides are among the most studied of these, with reviews covering design strategies for two-dimensional transition-metal nanosheets [81] and self-supported architectures [82].

The mechanistic question that connects these reviews is whether oxygen forms from adsorbed species on a metal site, known as the adsorbate evolution mechanism (AEM), or with the help of lattice oxygen, the lattice oxygen mechanism (LOM). Figure 4 sets the two side by side. In the

AEM column, the oxygen atoms come from water-derived intermediates on a metal site, so the scaling relations of Section 3.2 apply. In the LOM column, a lattice oxygen takes part in the O–O bond and is later refilled, which can bypass the scaling floor but ties activity to the stability of the lattice [77, 80]. A study of iron- and sulfur-modified nickel–iron oxyhydroxide reports that both pathways can operate on one catalyst, with iron promoting the AEM and sulfur exciting lattice oxygen [35]. The catalyst needs overpotentials of 251 ± 5 mV at 100 mA cm^{-2} and 291 ± 1 mV at 500 mA cm^{-2} and stays stable for more than 300 h. The 40 mV rise over a fivefold increase in current corresponds to an average slope of about 57 mV per decade between the two points (our calculation from the reported values). Table 6 condenses these points and links each one to the sources.

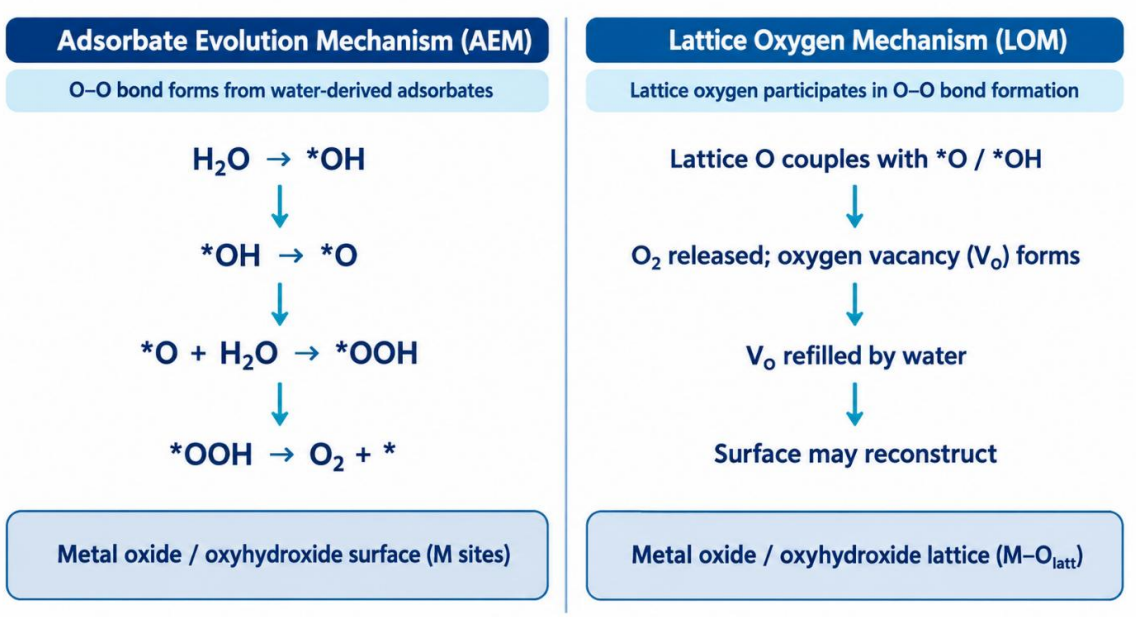

Figure 4. Schematic comparison of the adsorbate evolution mechanism (AEM, left) and the lattice oxygen mechanism (LOM, right) for oxygen evolution. Read each column from the bottom up (original schematic prepared for this review).

Table 6. Oxygen evolution mechanisms and what they mean for catalyst design.

Mechanism or strategy	Description	Design implication	Reference
AEM	O–O bond forms from water-derived adsorbates on metal sites	Limited by scaling relations among intermediates	[77, 80]
LOM	Lattice oxygen takes part in O–O bond formation	May bypass scaling; stability of the lattice becomes critical	[77, 80]
Combined AEM and LOM	Both pathways operate on one catalyst	Fe and S co-modulation of NiFe oxyhydroxide reported	[35]
Reconstruction	A precatalyst converts to an oxyhydroxide under OER	Active phase differs from the as-made material	[35, 40, 80]
Acidic stability	Ir and Ru catalysts under acidic conditions	Standardized durability protocols needed	[70, 76]
Layered double hydroxides	Ni, Co and Fe hydroxide nanosheets in alkaline media	Design of nanosheets and self-supported electrodes	[81, 82]
Seawater operation	Chlorine evolution competes with OER; chloride corrosion	Chloride-resistant and chlorine-suppressing designs	[36, 75]

An important caveat sits in the fourth row of Table 6. A cobalt- and ferrocene-based metal–organic framework, for instance, was shown to reconstruct into an oxyhydroxide during OER, so the framework acted as a precatalyst [40]. In numbers, the cobalt–ferrocene framework grown on nickel foam needed about 190 mV at 10 mA cm^{-2} in 1 M KOH and kept about 95 % of its activity after 24 h, while its metal nodes passed through two steps, Fe(III)-doped $Co(OH)_2$ at rest

and Fe-doped cobalt oxyhydroxide under OER [40]. When a paper attributes activity to the structure it started with, it is worth checking whether that structure was still present at the end of the test. Figure 5 shows the sequence we have in mind. The precatalyst changes under potential, the working state may be an oxyhydroxide or another phase, and the structure after the test may differ again, which is why the diagnostics at the bottom of the figure matter. The techniques named there are the subject of Section 6.

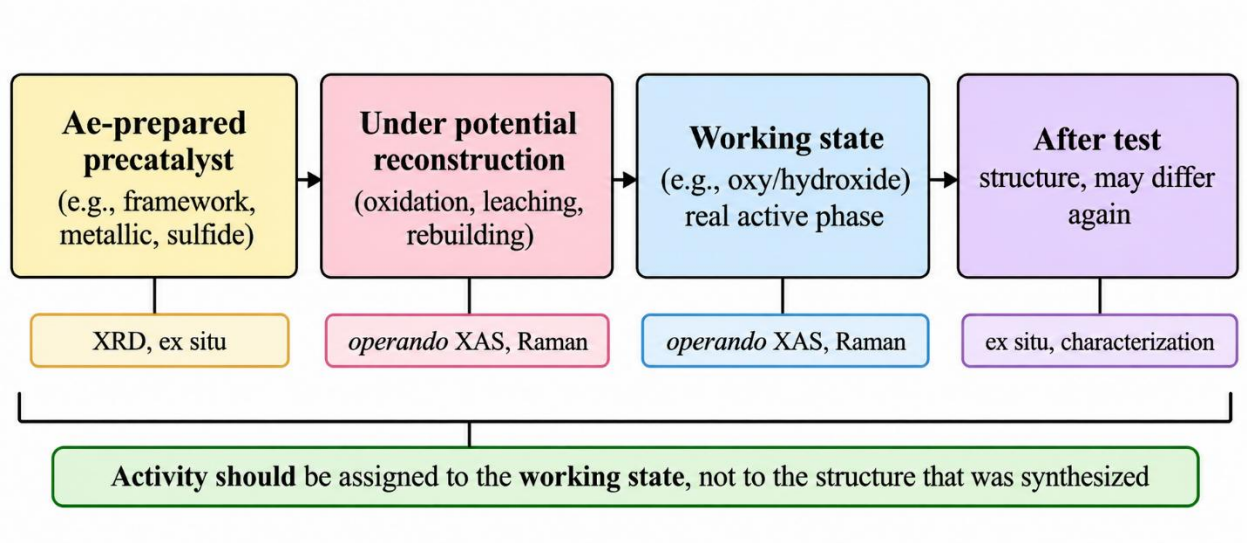

Figure 5. Conceptual sequence of catalyst reconstruction from as-prepared precatalyst to working state and post-test structure, with the type of measurement that can see each stage (original schematic prepared for this review).

4.3 Oxygen reduction reaction (ORR)

Oxygen reduction governs the cathode of fuel cells. Platinum-based catalysts remain the practical standard, and recent reviews concentrate on how to make them last, with attention to degradation mechanisms and stabilizing strategies [83, 84]. Atomically dispersed metal–nitrogen–carbon catalysts, particularly Fe–N–C, are the main platinum-group-metal-free alternative. Their activity has become competitive in half-cells, but reviews of their durability

describe metal leaching, carbon corrosion, protonation and flooding of micropores as persistent issues [85–87]. A two-electron route to hydrogen peroxide is the other branch of the reaction; the mechanisms, active sites and catalyst types are summarized in a recent review [88]. Figure 6 sketches the two competing routes: the four-electron route to water, with a standard potential of about 1.23 V versus the reversible hydrogen electrode, and the two-electron route to hydrogen peroxide at about 0.70 V. Which route a catalyst follows depends on whether the O–O bond of the *OOH intermediate is kept or broken, so one reaction can lead to two very different products.

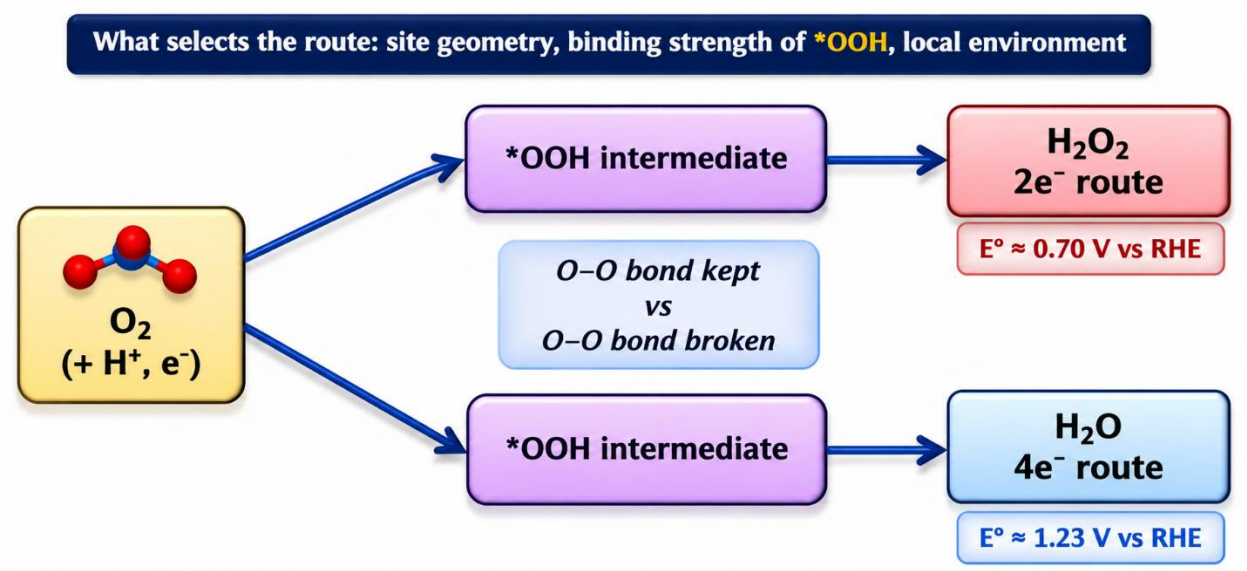

Figure 6. Two routes for oxygen reduction: the four-electron route to water and the two-electron route to hydrogen peroxide, with the factors that decide which route a catalyst follows (original schematic prepared for this review; for background see [88]).

4.4 Carbon dioxide reduction (CO_2RR)

CO_2 reduction can give carbon monoxide, formate, methane, ethylene, ethanol and other products. The metals differ in which product they favour, and a survey of traditional and newer benchmark catalysts tracks how this picture has developed [89]. Copper is the metal that makes multicarbon products, and membrane-electrode-assembly studies for ethylene review the reaction mechanism, catalyst design and the components of the assembly together [15]. Surface chemistry

is another handle: modification of copper with organic molecules is reviewed as a route to better C_{2+} selectivity and stability, since copper is the only metal that produces multicarbon products from CO_2 in aqueous electrolytes [37], and molecular amine catalysts have been surveyed for both homogeneous and heterogeneous operation [90]. Operating in acid is attractive because it avoids carbonate formation, and the review of acidic CO_2 electroreduction treats this as a systems problem that goes well beyond the catalyst [9]. In practice, the device-level issues described in Section 8, notably salt precipitation, decide how long a good catalyst can work [7, 8]. Process modeling and techno-economic analysis for CO_2 electroreduction have been reviewed as well [91].

4.5 Nitrate reduction to ammonia

Ammonia is a major chemical and a candidate fuel carrier. Nitrate reduction is attractive because nitrate is also a pollutant, so the reaction links ammonia production with water treatment. The recent reviews approach it from different angles: reaction mechanisms and materials [16, 17], carbon-based catalysts and their design strategies [18], copper-based catalysts [19], and catalyst design combined with electrolyte engineering and performance evaluation [92]. Wider surveys treat nitrogen and nitrate together as feedstocks for ammonia and distinguish two mechanisms, molecular–catalyst interaction and bond breaking with directional coupling [93]; framework-derived catalysts have been collected for both reactions [94]. Selectivity between ammonia and other nitrogen products is still the central practical question. Figure 7 shows why. Counting electrons per nitrogen atom, reduction to nitrite takes 2, to nitric oxide 3, to nitrous oxide 4, to nitrogen gas 5, to hydroxylamine 6 and to ammonia 8. Ammonia therefore needs the longest chain of steps and competes with several shorter, off-target exits, so the catalyst has to hold the intermediates on the surface until the chain is complete.

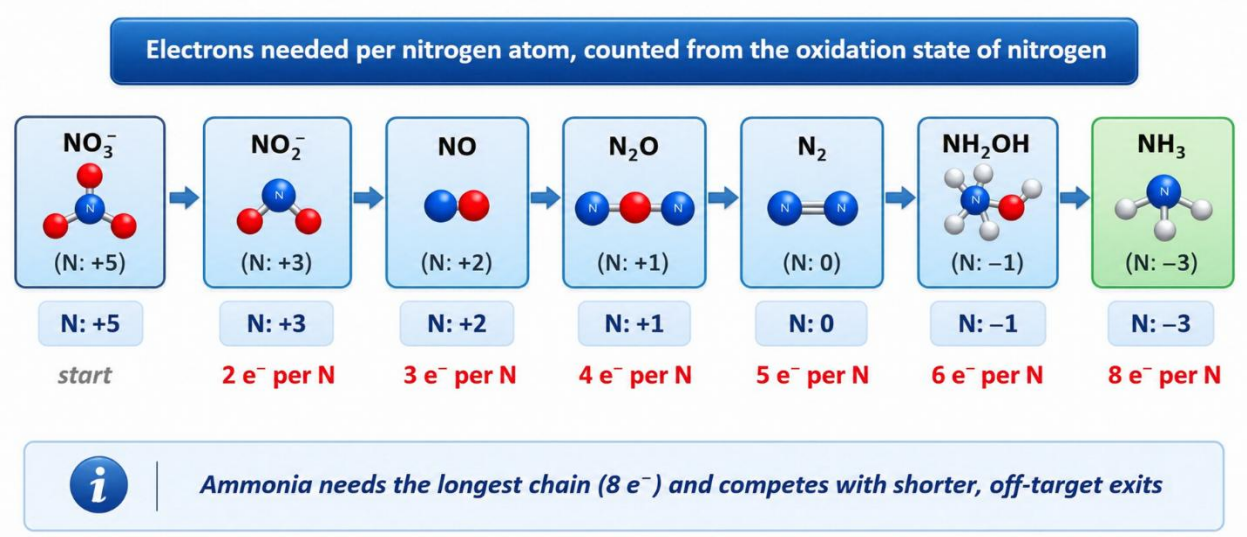

Figure 7. Electrons needed per nitrogen atom along the nitrate reduction ladder, from nitrate to nitrite, nitric oxide, nitrous oxide, nitrogen, hydroxylamine and ammonia (original schematic prepared for this review; for background see [16]).

Table 7 gathers the reactions covered in this section, with the reference catalysts, the newer catalyst families and the main open problem for each.

Table 7. Key electrocatalytic reactions, benchmark catalysts and open problems.

Reaction	Benchmark catalysts	Emerging catalyst families	Main open problem	Reference
HER	Pt	Phosphides, covalent organic frameworks, hetero-interfaces	Durability and replacement of Pt	[71–73]
OER	Ir and Ru oxides (acid); Ni–Fe (alkaline)	Mixed-metal oxides; reconstructing precatalysts	Acid stability; identity of the active phase	[40, 76, 80]
ORR	Pt and Pt alloys	Fe–N–C and other	Stability in	[83, 85, 87]

Reaction	Benchmark catalysts	Emerging catalyst families	Main open problem	Reference
		atomically dispersed sites	operating fuel cells	
$2e^-$ ORR	Various	Tailored active sites	Selectivity toward H_2O_2	[88]
CO_2RR	Ag, Au (CO); Cu (multicarbon)	Cu in membrane electrode assemblies; organic–Cu interfaces; single-atom sites	Selectivity, carbonate loss, salt precipitation	[9, 15, 37, 89]
NO_3RR	Cu-based	Carbon-based, Cu-based and framework-derived catalysts	Selectivity toward ammonia; electrolyte environment	[16, 18, 19, 92, 94]

5. Catalyst Design Families

5.1 Single-atom and dual-atom catalysts

Single-atom catalysts spread isolated metal atoms over a support, which maximizes the use of the metal and gives coordination environments that theory can handle. The recent review of single-atom engineering covers fundamentals and applications across water splitting, oxygen reduction, CO_2 reduction and ammonia synthesis [10]. Dual-atom catalysts put two metals next to each other so that different intermediates can bind at different atoms, which is one way to loosen the scaling relations described in Section 3.2 [11]. The weak point of these materials, as the fuel-cell literature shows, is durability. Reviews on Fe–N–C catalysts for fuel cells discuss how synthesis strategy and structure influence both activity and lifetime [86, 87]. Figure 8 shows the appeal of single atoms with a simple count. In a closed-shell fcc cluster, the share of atoms at

the surface is 92 % at 13 atoms, 76 % at 55 atoms, 52 % at 309 atoms and 39 % at 923 atoms (our calculation), and only the isolated atom reaches 100 %, which is why metal utilization approaches 100 % for single-atom catalysts. We see durability as the clearest example of the gap between half-cell activity and device relevance.

Single-atom catalysts have been studied most intensively for CO_2 reduction, and the reviews converge on one lesson: the coordination environment is as important as the metal. Strategies include regulating the central atom and its coordination [39], asymmetric coordination through low coordination, heteroatom coordination, dual-metal sites and the second coordination sphere [38], and a structure–performance view of single-metal-atom catalysts from theory and experiment [95]. Table 8 lines these strategies up.

Table 8. Strategies for tuning single-atom sites in CO_2 reduction, as described in recent reviews.

Strategy	**Idea**	**Reference**
Central-atom choice	Select the metal to set the main product	[39, 95]
Coordination regulation	Change the number and type of neighbouring atoms	[38, 39]
Asymmetric coordination	Break the symmetry of the M–N_4 site (low or heteroatom coordination, second sphere)	[38]
Dual-metal sites	Two adjacent metals bind different intermediates	[11, 38]

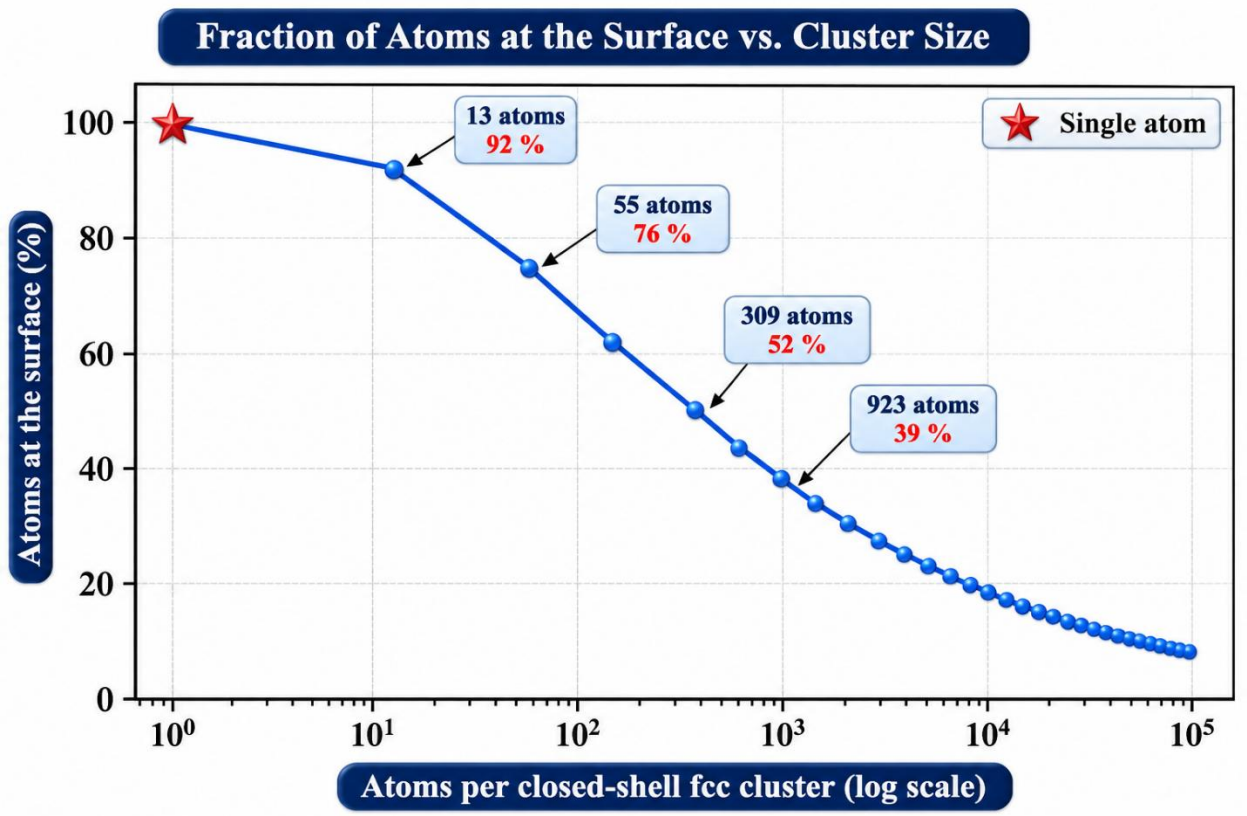

Figure 8. Share of atoms at the surface of closed-shell fcc clusters as a function of the number of atoms, calculated by the authors from the cuboctahedral magic numbers; the single atom, at 100 %, is marked with a star (original calculation; for background on single-atom catalysts see [10, 38]).

5.2 High-entropy and compositionally complex materials

High-entropy materials contain five or more elements in a single phase. The idea is that the large number of local environments produces many different surface sites, so that something close to the volcano peak of Figure 3 can be found by composition tuning. Table 9 lists the recent reviews that we used. They treat high-entropy alloys and their derived compounds [13], water-splitting applications [96], oxides [14], hydrogen evolution [97] and the combination of oxygen reduction and hydrogen evolution [98]. One review focuses on thermodynamic design and computational modeling [99]. A fair reading of this literature is that gains in activity are well

documented, whereas the claim that configurational entropy itself is responsible requires controlled comparisons that are not always present.

Table 9. Recent open-access reviews of high-entropy electrocatalysts used in this article.

Review	Focus	Reference
High-entropy alloys and derived compounds	Understanding, preparation and application	[13]
High-entropy alloys for water splitting	Catalyst design for HER and OER	[96]
High-entropy oxides	Advances, challenges and prospects as electrocatalysts	[14]
High-entropy alloys for HER	Recent progress	[97]
High-entropy alloys for ORR and HER	Recent advances and perspectives	[98]
Thermodynamic design and modeling	Computational strategies for high-entropy alloys	[99]
High-entropy nanomaterials	General overview for electrocatalysis	[12]

5.3 Framework-derived catalysts

Covalent organic frameworks offer tunable porosity and designable active sites, and they have been explored as water-splitting electrocatalysts, both with and without metal centres [72]. Metal–organic frameworks bring a complication already seen in Section 4.2: under operating potentials many of them transform. The cobalt- and ferrocene-based framework mentioned there rearranged into an oxyhydroxide during the oxygen evolution reaction [40]. Frameworks and their derivatives are also being applied to ammonia electrosynthesis, from both nitrogen and

nitrate [94]. For a reader, this means that framework papers should be judged on what the material looks like after the test.

5.4 Heterostructures and interfaces

Putting two phases in contact can create sites that neither phase has alone, and a review of nanoscale hetero-interfaces for water splitting collects the approaches [73]. As with the other families, separating a true interface effect from a change in surface area or from reconstruction needs operando evidence, which is the topic of Section 6.

5.5 Molecular and hybrid catalysts

Molecular catalysts, such as metal porphyrins, give very well defined active sites. A review of immobilization strategies for porphyrin-based catalysts shows how attaching them to electrodes opens the way to CO_2 reduction in practical cells [100]. The remaining question is long-term stability once the molecule is anchored to a surface and exposed to current.

Table 10 summarizes the five families. The comparison shows that no family is free of a limitation: each one gains in one dimension and loses in another.

Table 10. Catalyst design families, their principle, strengths and limits.

Family	Design principle	Strength	Limitation	Reference
Single and dual atom	Isolated or paired metal sites on supports	High metal utilization; well-defined sites	Durability under operating conditions	[10, 11, 38, 87]
High entropy	Many elements in one phase	Large composition space	Role of entropy hard to isolate	[13, 99]
Framework-derived	Porous, designable frameworks	Tunable structure	Reconstruction under potential	[40, 72, 94]

Family	Design principle	Strength	Limitation	Reference
Heterostructure	Engineered interfaces	Synergistic sites	Interface effect versus surface area	[73]
Molecular	Defined coordination complexes	Mechanistic clarity	Stability after immobilization	[100]

6. Operando Characterization

One lesson from the last few years is that a catalyst as synthesized is often not the catalyst that works. Surfaces oxidize, dissolve and rebuild themselves under potential, which is why the OER precatalyst examples in Section 4.2 matter so much. Operando methods, which watch the working material while recording its activity, are therefore the main way to link a structure to a result. Reviews of in situ characterization in electrocatalysis describe how the techniques can follow nanoscale structure alongside performance [46].

X-ray absorption spectroscopy reports the oxidation state and the local coordination around a metal, and its use for electrocatalysts under operating conditions has been reviewed in detail [41]. Vibrational methods target the adsorbates themselves; time-resolved in situ vibrational spectroscopy is a route to observing intermediates, though it brings its own challenges [42], and infrared spectroscopy has been reviewed specifically for CO_2 reduction in terms of theory, practice and difficulties [101]. For batteries, the same idea carries over: a recent review on interphases and interfaces of battery materials at the nanoscale shows how much of cell behaviour is decided in layers a few nanometres thick [57]. Figure 9 maps the techniques we discuss against the information they mainly give: X-ray absorption for oxidation state and local coordination, vibrational spectroscopy for adsorbed species, X-ray diffraction for crystal

structure, electron microscopy for morphology and mass spectrometry for gas products. Table 11 lists the techniques that we cite and what each one can and cannot tell us.

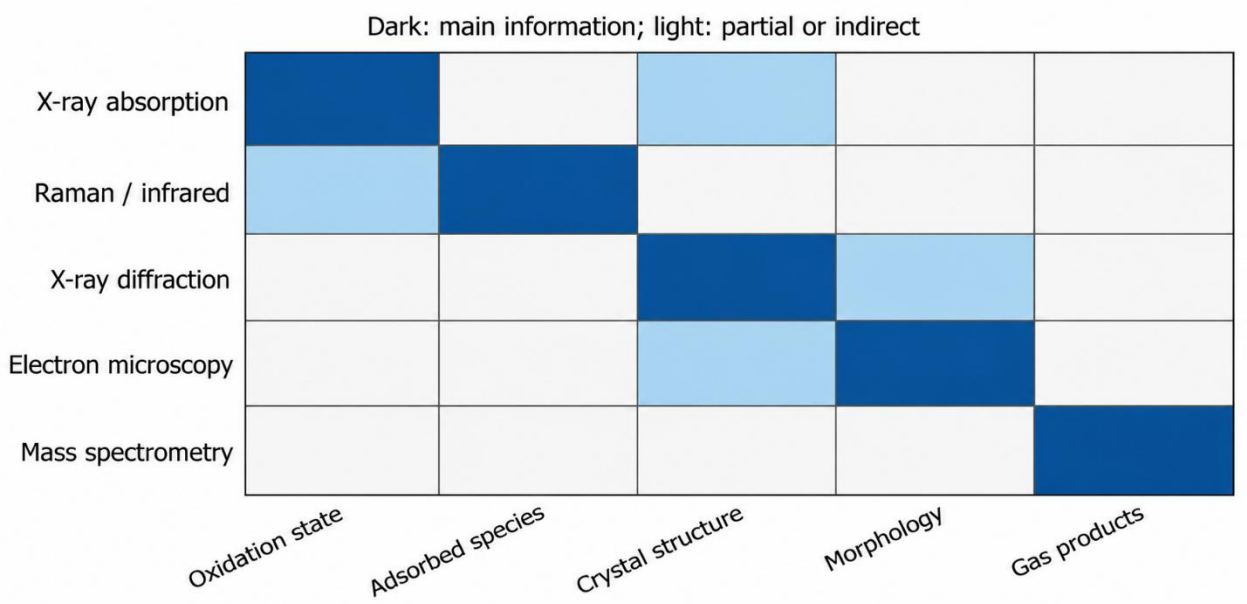

Figure 9. Operando and in situ techniques mapped against the main information they provide (original schematic prepared for this review; for background see [41, 42, 46]).

Table 11. Operando and in situ techniques cited in this review.

Technique	Information	Typical use	Key limitation	Reference
X-ray absorption spectroscopy	Oxidation state; local coordination	Single-atom and oxide catalysts	Averages over the sample	[41]
Vibrational spectroscopy (infrared, Raman)	Adsorbed intermediates	CO_2 reduction and other reactions	Signal interpretation; surface selectivity	[42, 101]
Nanoscale in situ methods	Structure alongside	Electrocatalyst structure studies	Cell may differ from a working	[46]

Technique	Information	Typical use	Key limitation	Reference
	performance		device	
Interface and interphase analysis	Layers at battery electrodes	Solid-electrolyte and electrode interfaces	Not always fully operando	[57]

The most important weakness of Table 11 is shared by all rows. Different techniques probe different depths and timescales, and the measurement cell often differs from a working device in current density and mass transport. For this reason it is good practice to combine at least two complementary methods and to check that the cell reproduces device-relevant activity, a point that links directly to the device discussion in Section 8.

7. Data-Driven and Machine-Learning Approaches

Machine learning now has a regular place in catalyst research. The overview by Steinmann, Wang and Seh describes how it can speed up the discovery and optimization of electrocatalysts [20], and a recent review follows machine-learning approaches for water-splitting catalysts across the catalyst life cycle, with green hydrogen production as the goal [21]. Physics-informed and interpretable models try to make predictions understandable to chemists [22], and machine-learning-assisted design of low-dimensional hydrogen-evolution catalysts is a concrete application [23]. In batteries, machine learning has been applied to predict properties of lithium solid electrolytes [58]. For CO_2 the scope is wider: a recent review covers machine learning for both capture solvents and electrochemical conversion catalysts, and argues that coupled capture-and-conversion systems will need the two to be combined [102]. Figure 10 groups these uses into four tasks: surrogate models that replace costly calculations, learned potentials that approximate atomistic energies, experiment assistants that interpret spectra and images, and automated platforms that plan, synthesize and test candidates. Table 12 lists the sources.

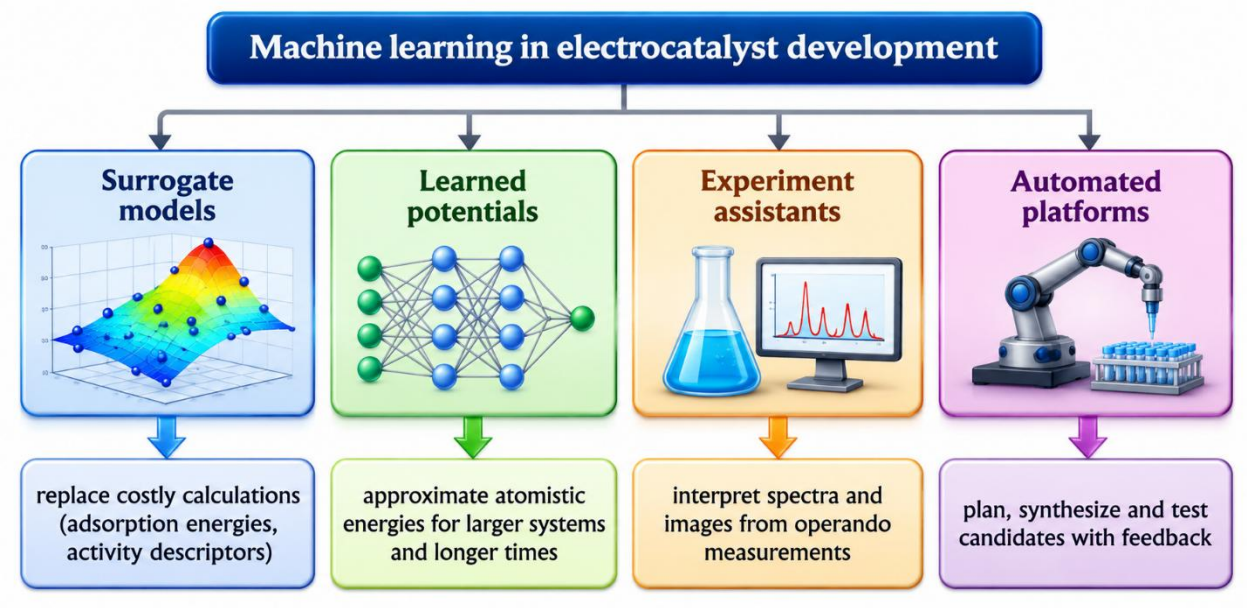

Figure 10. Four ways in which machine learning enters electrocatalyst development: surrogate models, learned potentials, experiment assistants and automated platforms (original schematic prepared for this review; for background see [20, 21, 22]).

Table 12. Machine-learning approaches relevant to electrocatalysts and battery electrolytes.

Approach	Application	Reference
Machine-learning models and surrogates	Accelerating electrocatalyst discovery and optimization	[20]
Machine learning for water-splitting catalysts	Design along the catalyst life cycle	[21]
Interpretable physics-informed models	Electrocatalyst development with interpretability	[22]
Machine-learning-assisted design	Low-dimensional HER catalysts	[23]
Property prediction	Lithium solid-state electrolytes	[58]

Approach	Application	Reference
Machine learning for CO_2	Capture solvents and conversion catalysts	[102]

Two cautions apply. The first is that a model is only as good as its data, and the data used for electrocatalysis are small, uneven and reported in inconsistent ways, as the discussion of metrics in Section 3.5 suggests. The second is that descriptors computed for an idealized surface can miss the effects of electrolyte and field described in Section 3.3. Figure 11 shows the arrangement that many groups now aim for. Candidate selection by a model feeds synthesis and testing, operando measurements add mechanistic information, and the results flow back into the model. The loop works only if each step produces data that the next step can trust, which brings us back to reporting standards.

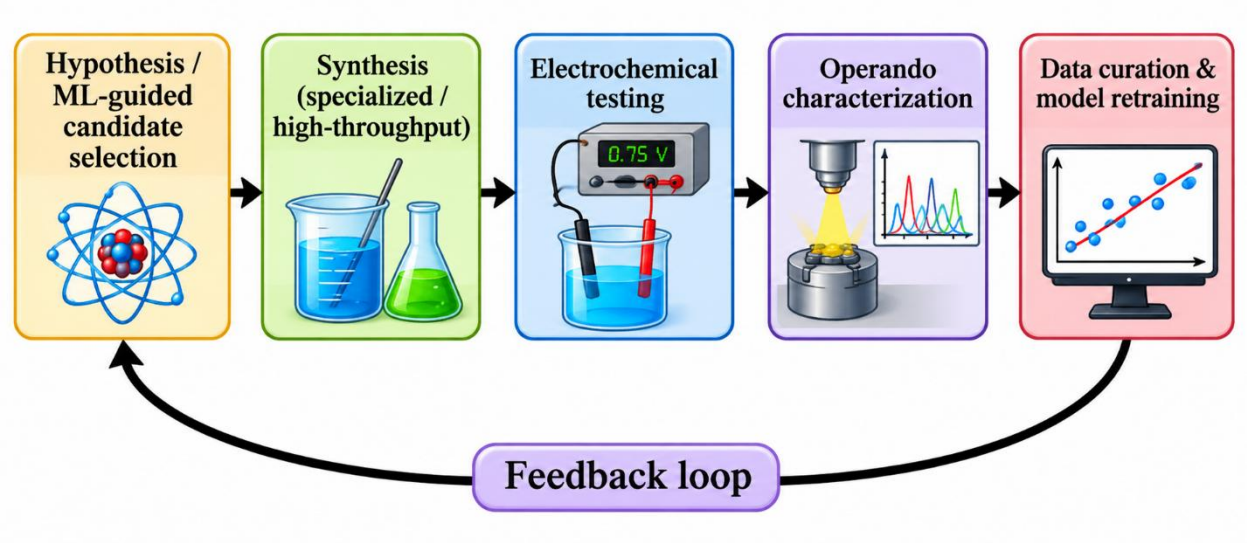

Figure 11. Closed-loop, data-driven workflow for electrocatalyst development: candidate selection, synthesis, electrochemical testing, operando characterization and data curation, with feedback to the model (original schematic prepared for this review).

8. From Half-Cells to Devices

8.1 The performance gap

Most catalyst papers report results from three-electrode half-cells at modest current density and for short periods. A working electrolyzer or fuel cell operates under very different conditions, and the recent review of platinum-group-metal OER catalysts makes the point that differences between test setups and protocols prevent fair comparison of stability results [70]. This is the reason Figure 2 matters: a catalyst has to function inside a layered stack, together with a membrane, an ionomer and a porous transport layer, not as an isolated powder.

8.2 Electrodes, membranes and water management

In CO_2 electrolysis, the membrane electrode assembly with a gas-diffusion electrode has made industrially relevant current densities (above 200 mA cm^{-2}) reachable [7], but it exposes a new failure mode. Carbonate salts can precipitate in the gas-diffusion layer, and flooding follows. Figure 12 illustrates the failure mode: CO_2 reduction at the cathode generates hydroxide, hydroxide converts CO_2 to carbonate, and carbonate with the cations in the electrolyte forms precipitates that accumulate in the gas-diffusion layer. A paper on zero-gap cells describes the challenges and operational strategies for preventing salt precipitation [7], and another reports strategies to mitigate it in zero-gap electrolyzers producing carbon monoxide [8]. The review on acidic CO_2 reduction includes the electrode structure and the reactor in its list of design variables [9], and the review on copper catalysts in a membrane electrode assembly covers the components and operation of the assembly [15]. For water electrolysis, AEM and PEM designs trade catalyst cost against membrane and ionomer durability [4–6]. Inside the catalyst layer, the ionomer is the quiet partner of the catalyst: a review of hydrocarbon ionomeric binders surveys what ionomers must do in the electrodes of fuel cells and electrolyzers and how hydrocarbon ionomers might be designed [34], and a review of oxygen transport in catalyst layers explains how structure, carbon

support and ionomer design can reduce the transport resistance in fuel cells, with ideas for water-electrolyzer anodes [69]. These layers are the middle blocks of Figure 2, which is why a catalyst cannot be judged without them.

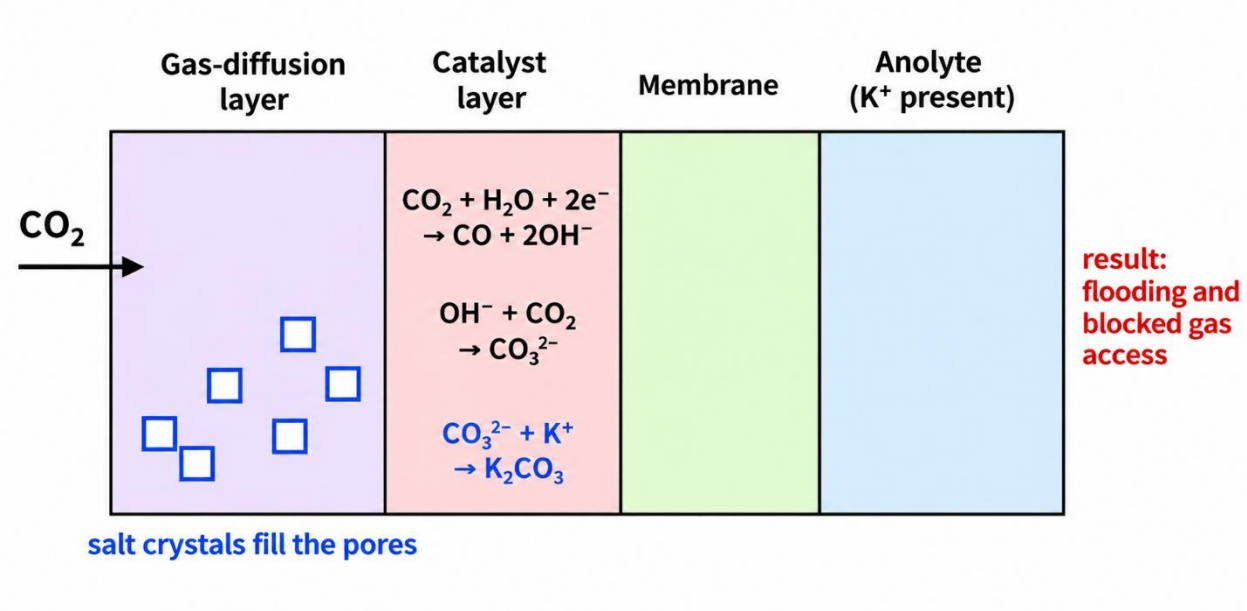

Figure 12. Salt precipitation in a zero-gap CO_2 electrolyzer: reaction at the cathode, carbonate formation, precipitation in the gas-diffusion layer, and the resulting flooding (original schematic prepared for this review; for background see [7, 8]).

8.3 Degradation and durability

Degradation differs from device to device, and Table 13 brings together what we found. In PEM water electrolysis, degradation studies with four accelerated stress protocols point to platinum dissolution and iridium oxidation as key pathways [43]; the targets quoted there, set by the U.S. Department of Energy, are a lifetime of 80,000 h and a platinum-group-metal loading of 0.5 mg cm^{-2} by 2026 [43]. In fuel cells, durability of platinum-based catalysts is the focus of recent reviews [83, 84], and Fe–N–C catalysts add metal leaching, carbon corrosion, protonation and micropore flooding to the list [85, 86]. Salt precipitation and flooding dominate the CO_2 row [7, 8]. In lithium-based cells, failure modes range from interface breakdown to thermal events [50],

while nanoscale interphase studies explain the slow growth of resistive layers [28, 57]. In vanadium flow batteries, membranes are again the issue, since crossover and membrane properties determine lifetime [66, 67].

Table 13. Degradation and durability issues by device, with the sources that discuss them.

Device or material	Reported issue	Reference
PEM water electrolyzer	Pt dissolution and Ir oxidation under accelerated stress tests; protocol variability	[43, 70]
PEM fuel-cell cathode (Pt-based)	Durability of Pt catalysts in operation	[83, 84]
Fe–N–C catalysts	Metal leaching, carbon corrosion, protonation, micropore flooding	[85–87]
CO_2 electrolyzer (zero-gap MEA)	Salt precipitation and flooding	[7, 8]
Lithium-ion cell	Failure modes from materials to systems; interphase evolution	[50, 57]
Ni-rich cathode	Surface degradation, cation mixing, microcracks, gas release	[31, 48]
PEM electrolyzer components	Low-iridium operation, membrane durability, transport layers	[33, 68]
Sulfide solid-state cell	Resistive interphases at electrodes	[28, 29]
Vanadium flow battery	Crossover and membrane properties	[66, 67]

A single pattern emerges from Table 13: in each device the weak link is an interface or a transport layer, and not the bulk activity that most catalyst papers report. This is the same message as Table 4, now seen from the failure side.

8.4 Cost and life-cycle considerations

A catalyst's relevance depends on cost factors that lie outside the catalyst. The review on anion-exchange-membrane electrolyzers notes that conventional PEM electrolysis relies on critical raw materials, which is one of the reasons to look for alternatives [4]. For CO_2 electroreduction, process modeling, techno-economic assessment and life-cycle assessment have been reviewed [91]. We found fewer open-access reviews that meet our criteria on water-electrolysis economics, and this is one place where the present review is thinner than we would like. Readers who plan to use these arguments in a proposal should consult dedicated techno-economic studies.

9. Quantitative Synthesis of Reported Findings

The sections above quote many numbers. This section puts them side by side, because the comparison says more than any single value. Figure 13 plots three groups of them. Panel (a) shows how widely the room-temperature conductivities of inorganic solid electrolytes spread: the oxide, sulfide and halide ranges overlap, and the span from the lowest to the highest value is about three orders of magnitude [27]. Panel (b) shows the operating windows of four electrolyzer technologies; the three low-temperature technologies sit between 40 and 90 °C, while solid-oxide cells operate at 600–850 °C, which shifts the materials problem from catalyst activity to thermal durability [33]. Panel (c) collects two oxygen-evolution results from alkaline media. They belong to different catalysts, so the points are not a ranking; they show instead the scale of overpotential at current densities from 10 to 500 mA cm^{-2} [35, 40].

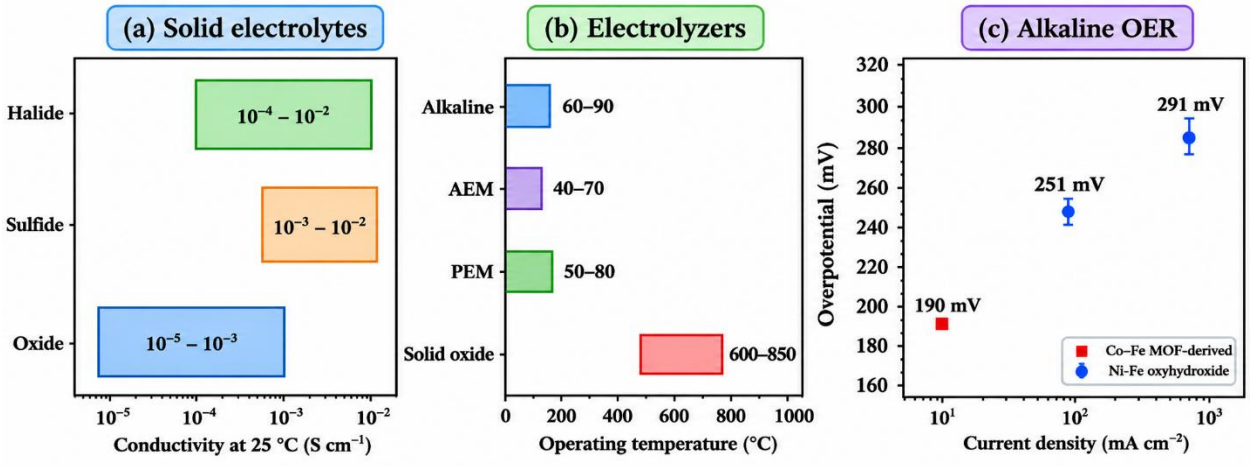

Figure 13. Quantitative ranges reported in the reviewed literature. (a) Room-temperature conductivity ranges of oxide, sulfide and halide solid electrolytes [27]. (b) Operating temperature windows of liquid-alkaline, anion-exchange-membrane, proton-exchange-membrane and solid-oxide electrolyzers [33]. (c) Reported oxygen-evolution overpotentials of a nickel–iron oxyhydroxide [35] and a cobalt–ferrocene framework-derived catalyst [40]; different catalysts, shown together only to indicate scale (original chart prepared from the cited values).

Table 14 lists the numerical findings behind the figure and the rest of the review, with the conditions under which each value was reported.

Table 14. Numerical findings reported in the reviewed literature.

Topic	Quantity	Reported value	Conditions or note	Reference
Oxide solid electrolyte	Ionic conductivity	10^{-5} to 10^{-3} S cm^{-1}	25 °C	[27]
Sulfide solid electrolyte	Ionic conductivity	10^{-3} to 10^{-2} S cm^{-1}	25 °C	[27]
Halide solid electrolyte	Ionic conductivity	10^{-4} to 10^{-2} S cm^{-1}	25 °C	[27]

Topic	Quantity	Reported value	Conditions or note	Reference
Ni-rich layered cathode	Nickel content	at least 80 %	Definition of "Ni-rich" used in the review	[30]
Zinc–air battery	Energy density	up to 1086 Wh kg^{-1}	As reported in the review	[32]
Liquid alkaline electrolyzer	Operating temperature	60–90 °C	Materials review	[33]
AEM electrolyzer	Operating temperature	40–70 °C	Materials review	[33]
PEM electrolyzer	Operating temperature	50–80 °C	Materials review	[33]
Solid-oxide electrolyzer	Operating temperature	600–850 °C	Materials review	[33]
PEM fuel cell	Platinum loading	0.4 mg cm^{-2}	After introduction of ionomer thin-film electrodes	[34]
PEM water electrolyzer	Lifetime and loading targets	80,000 h; 0.5 mg PGM cm^{-2} by 2026	U.S. DOE targets quoted in the study	[43]
Ni–Fe oxyhydroxide (OER)	Overpotential	251 ± 5 mV at 100 mA cm^{-2}; 291 ± 1 mV at 500 mA cm^{-2}	Alkaline media; stable for more than 300 h	[35]
Co–Fc	Overpotential	about 190 mV at 10	1 M KOH, nickel foam	[40]

Topic	Quantity	Reported value	Conditions or note	Reference
framework-derived catalyst (OER)	and retention	mA cm^{-2}; about 95 % activity after 24 h		
Seawater	Chloride concentration	about 0.5 M	Allows chlorine evolution to compete with OER	[36]
Zero-gap CO_2 electrolyzer	Current density	above 200 mA cm^{-2}	Industrially relevant range in GDE and MEA cells	[7]
Single-atom catalyst	Atom utilization	almost 100 %	Isolated metal sites	[38]
Vanadium flow battery membranes	Membranes compared	8 commercial membranes; 5 properties	Chemical stability, mechanical strength, conductivity, permeability, swelling	[67]

Three readings follow from Table 14. First, the numbers describe the best laboratory results, and they come from very different test durations. The longest stability test in the table is more than 300 h [35], which is under 0.4 % of the 80,000 h lifetime targeted for PEM electrolyzers [43]; the two numbers come from different devices, so the ratio shows the scale of the gap and not a measured shortfall. Second, the two OER catalysts share one feature that the table does not show: both are oxyhydroxides formed during operation from a precatalyst [35, 40], so the reported overpotentials belong to the working state. Third, the most useful numbers for practice,

such as current densities above 200 mA cm^{-2} and platinum-group-metal loadings of 0.4–0.5 mg cm^{-2}, are device-level quantities [7, 34, 43], while most catalyst papers report only half-cell values.

10. Challenges and Outlook

Looking across the sections, five points seem to us the most useful.

Interfaces dominate. In solid-state batteries the contact between solid electrolyte and electrode is the principal obstacle [2, 28], and in electrolyzers the cell stack and its transport layers decide durability [7, 43]. Better operando probes and interface-aware models are the most direct route forward [46, 57].

Reporting must improve. Normalization, product quantification and test duration vary between papers, and this limits comparison [44, 45]. Shared protocols and open data would improve the reliability of the field and also make machine-learning models more useful [20].

Reconstruction needs to be taken seriously. Many catalysts are precatalysts, as the OER examples show [35, 40], and claims about structure–activity relations should refer to the working state of the material.

Catalysts should be tested in devices early. Half-cell work is essential for mechanisms, but a promising material should be tested in a membrane electrode assembly at relevant current density before conclusions about practical value are drawn [15, 70].

Material supply and cost shape what can scale. The reliance of PEM devices on critical raw materials is one driver of AEM research [4, 6], and the same reasoning applies to single-atom and high-entropy catalysts that try to replace platinum-group metals [10, 13].

Synthesis: an interface matrix

Table 15 brings the sections together. Each row names a device or material, the interface where it tends to fail, the diagnostic that can see the failure, and the strategy that reviews propose. Read it

alongside Figure 14, which draws the same hotspots as a map. The table is deliberately short: it records only what the cited reviews support, and the empty spaces are the gaps this review set out to expose.

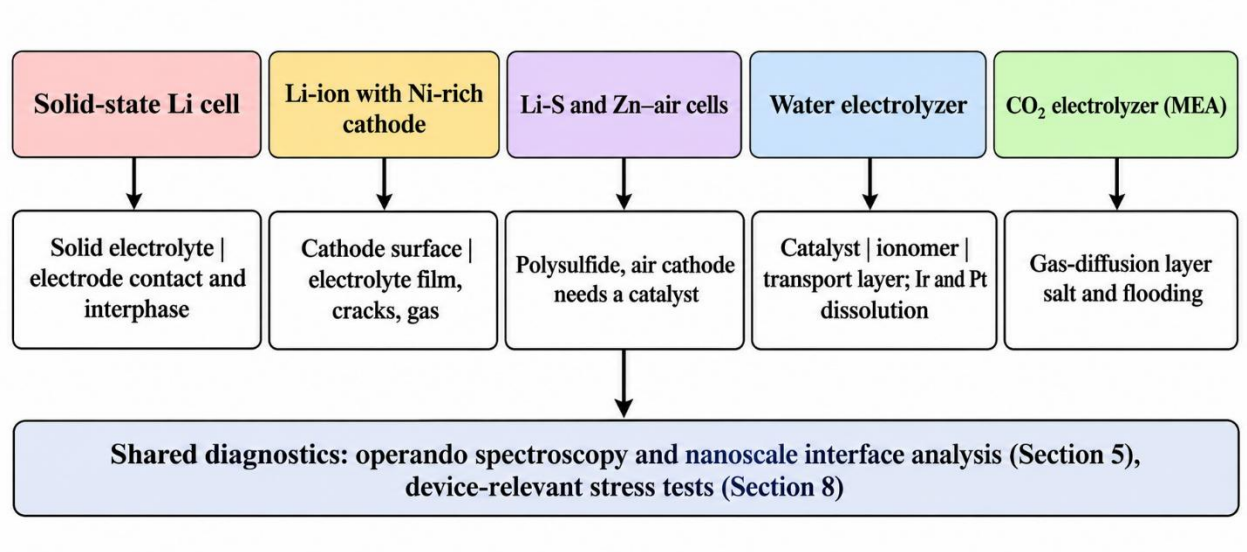

Figure 14. Interface hotspots across the devices discussed in this review, with the shared diagnostics that can inspect them (original schematic prepared for this review).

Table 15. Interface matrix: where each device or material fails, how it can be diagnosed, and what has been proposed.

Device or material	Interface hotspot	Diagnostic	Proposed strategy	Reference
Solid-state Li cell	Solid electrolyte against electrode	Nanoscale interphase analysis	Interlayers, composites, stack-pressure management	[52, 53, 57]
Sulfide solid electrolyte	Against electrodes and moisture	Interface and interphase studies	Interface engineering; handling control	[28, 29]

Device or material	Interface hotspot	Diagnostic	Proposed strategy	Reference
Ni-rich cathode	Cathode surface against electrolyte	Post-mortem and surface analysis	Coating, doping, single crystals	[30, 31]
OER precatalyst	Catalyst surface against electrolyte	Operando X-ray absorption and vibrational spectroscopy	Treat the working state as the catalyst	[35, 40, 41]
CO_2 electrolyzer	Gas-diffusion layer and catalyst layer	Cell-level stress tests	Salt-precipitation mitigation	[7, 8]
PEM electrolyzer	Catalyst, ionomer and porous transport layer	Accelerated stress tests	Low-Ir design; transport-layer engineering	[33, 43]

Research priorities

The reviews we have read point to a short list of priorities. Table 16 states each one with the reason and the kind of evidence that would settle it.

Table 16. Research priorities that follow from this review.

Priority	Reason	Evidence that would settle it	Reference
Standardized durability tests	Stability results cannot be compared across laboratories	Shared accelerated stress protocols for catalysts and devices	[44, 70]
Working-state	Many catalysts are	Operando structure paired	[35, 40]

Priority	Reason	Evidence that would settle it	Reference
structure	precatalysts	with activity in the same cell	
Device-relevant CO_2 tests	Salt precipitation and flooding appear only in cells	Long tests in membrane electrode assemblies	[7, 8]
Catalyst–ionomer co-design	Ionomer and oxygen transport limit catalyst use	Catalyst-layer studies with matched ionomers	[34, 69]
Open, standardized data	Machine learning needs consistent reporting	Shared data formats for activity and conditions	[20, 45]

11. Conclusions

This review set out to show that cells and catalysts share one limiting factor, and the collected data support that reading. Inorganic solid electrolytes conduct from 10^{-5} to 10^{-2} S cm^{-1} [27], yet reviews identify the contact between electrolyte and electrode, not bulk conductivity, as the main obstacle in solid-state batteries [1, 2, 52]. Electrolyzers work in windows of 40–90 °C or 600–850 °C [33], and in PEM cells accelerated stress tests point to platinum dissolution and iridium oxidation as key degradation routes [43]. In alkaline oxygen evolution, a nickel–iron oxyhydroxide delivers 100 and 500 mA cm^{-2} at 251 and 291 mV, an average slope of about 57 mV per decade between the two points, and stays stable for more than 300 h [35]; a cobalt–ferrocene framework needs about 190 mV at 10 mA cm^{-2} and keeps about 95 % of its activity after 24 h [40]. In both cases the active phase is an oxyhydroxide formed during operation, so activity has to be assigned to the working state.

The gap to practice is large when written in numbers. The longest laboratory stability test quoted here, over 300 h [35], is under 0.4 % of the 80,000 h lifetime targeted for PEM water electrolyzers [43], and CO_2 electrolyzers that reach more than 200 mA cm^{-2} still fail by salt precipitation [7, 8]. Single-atom catalysts approach 100 % atom utilization [38], but their

durability in fuel cells and the role of configurational entropy in high-entropy materials remain open questions [87, 99].

Three actions follow. Activity should be reported with clear normalization and product quantification [44, 45]; catalysts should be tested in membrane electrode assemblies at relevant current density and duration [7, 8, 43]; and operando measurements should be combined with machine learning to link structure and activity in the working state [20, 41]. These conclusions are limited by the design of this review, which is a narrative selection of 102 open-access sources and quotes numbers as reported by their authors under different conditions.

Abbreviations: AEM, adsorbate evolution mechanism (in Sections 4 and 6) or anion-exchange membrane (in Sections 2 and 8); CO_2RR, CO_2 reduction reaction; HER, hydrogen evolution reaction; LOM, lattice oxygen mechanism; MEA, membrane electrode assembly; NO_3RR, nitrate reduction reaction; OER, oxygen evolution reaction; ORR, oxygen reduction reaction; PEM, proton-exchange membrane; PEMWE, PEM water electrolyzer; SAC, single-atom catalyst.

Declarations

Author contributions: A.B.A.B. conceptualized the review, carried out the literature search and data extraction, prepared the figures and tables, and wrote the original draft. R.S. supervised the work, contributed to the interpretation of the findings, and reviewed and edited the manuscript. Both authors read and approved the final manuscript.

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