VSB TECHNICAL UNIVERSITY OF OSTRAVA | CENTRE FOR ENERGY AND ENVIRONMENTAL TECHNOLOGIES | ENERGY RESEARCH CENTRE

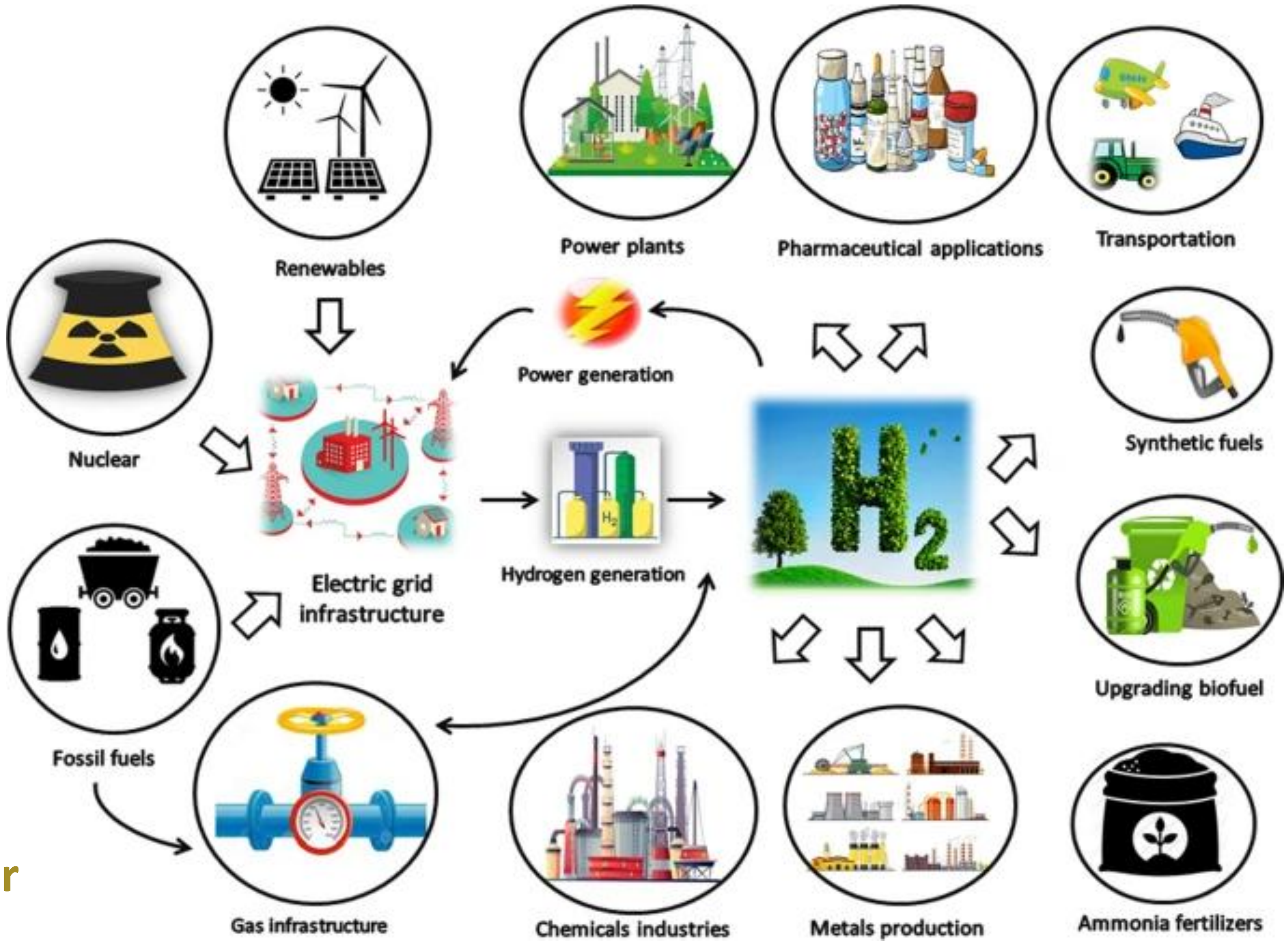
New directions and perspectives in membrane electrode assemblies for water electrolysis

prof. Daniela Plachá, Ph.D.
Energy Research Centre, VSB-TU of Ostrava

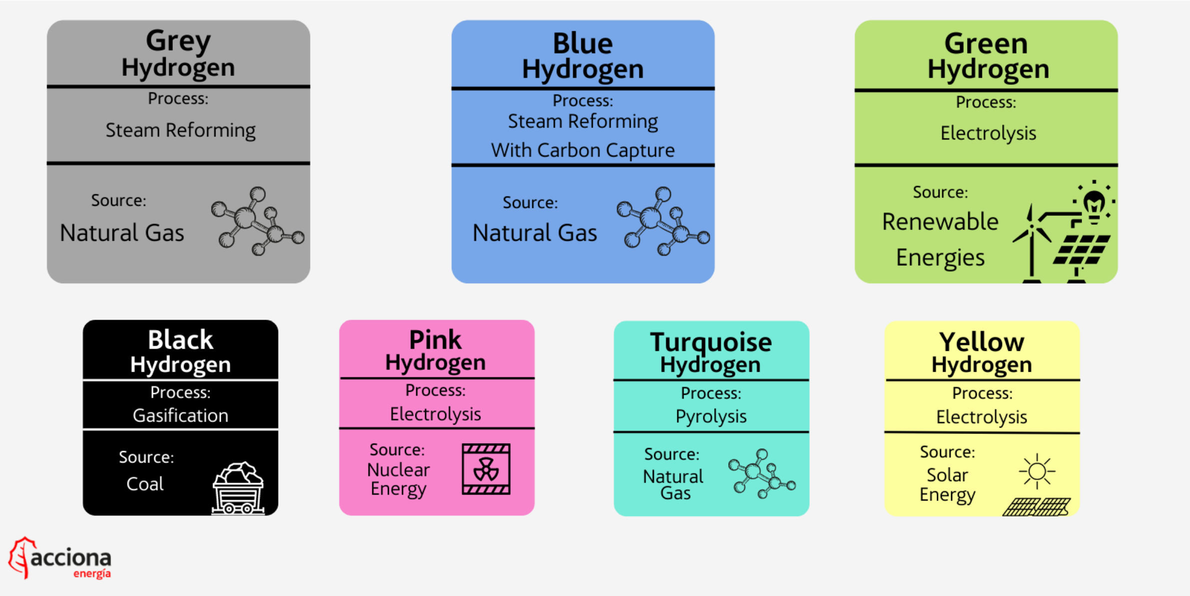
Importance of hydrogen

- **Chemical feedstock**
- **Metal production**
- **Energy storage**
- **Energy carrier**
- **Fuels**
- **Transportation**

Decarbonisation of industrial processes and economic sector

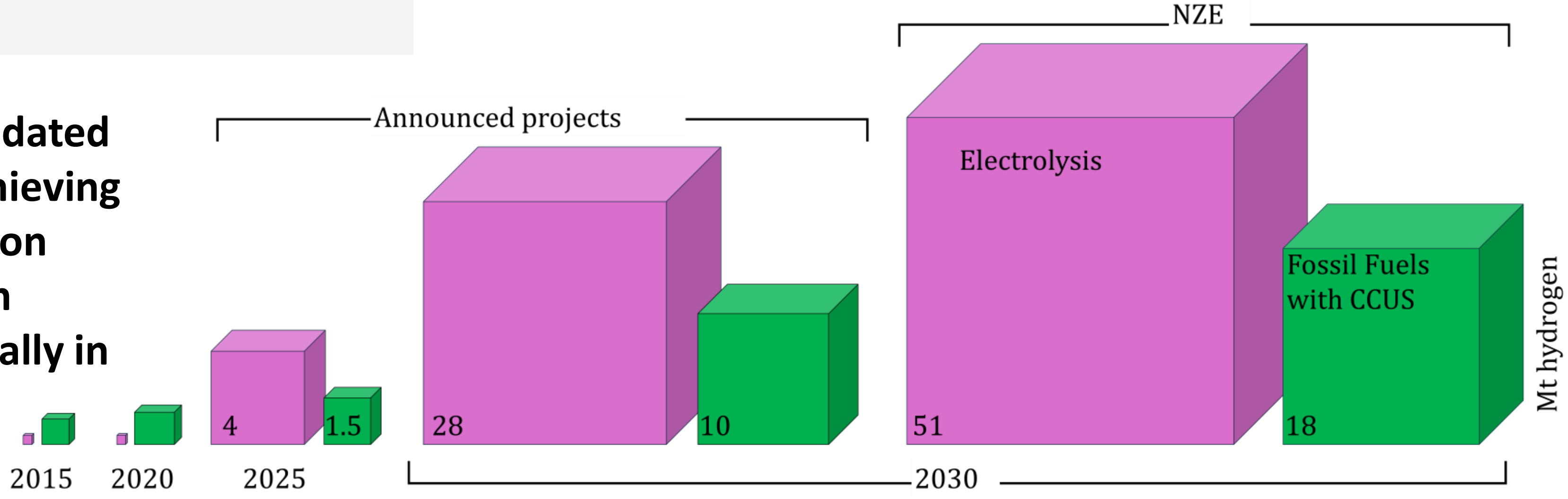


Hydrogen production



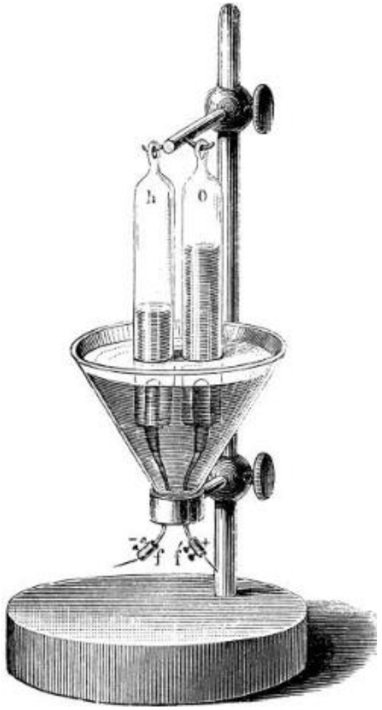
Classification of hydrogen according to extraction processes

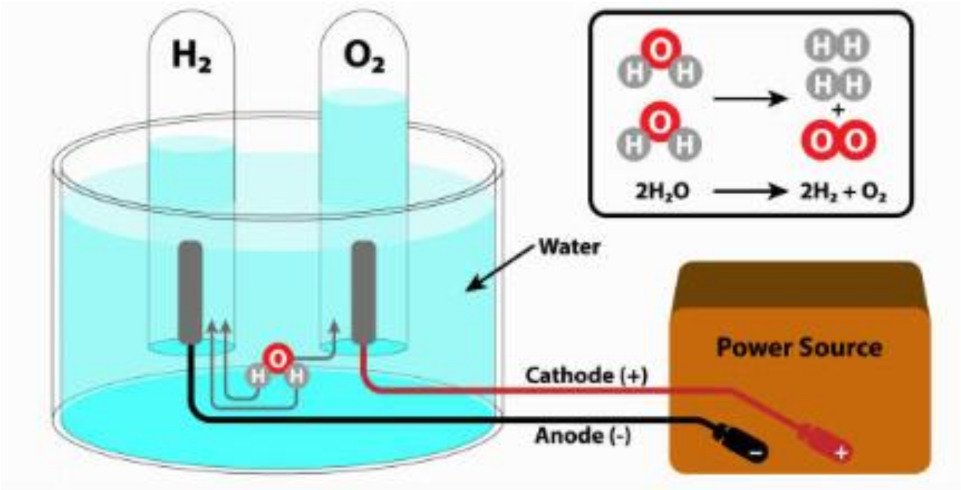
The International Energy Agency's updated roadmap outlines the pathway to achieving net zero emissions by 2050, focusing on reducing environmental impacts from traditional energy production, especially in hydrogen derived from fossil fuels.



IEA, Net Zero Roadmap: A Global Pathway to Keep the 1.5 °C Goal in Reach - 2023 Update. 2023

Electrolysis – water splitting $2H_2O \longrightarrow 2H_2 + O_2$





1789 van Troostwijk and Deiman – first generation of H_2 by electrolysis

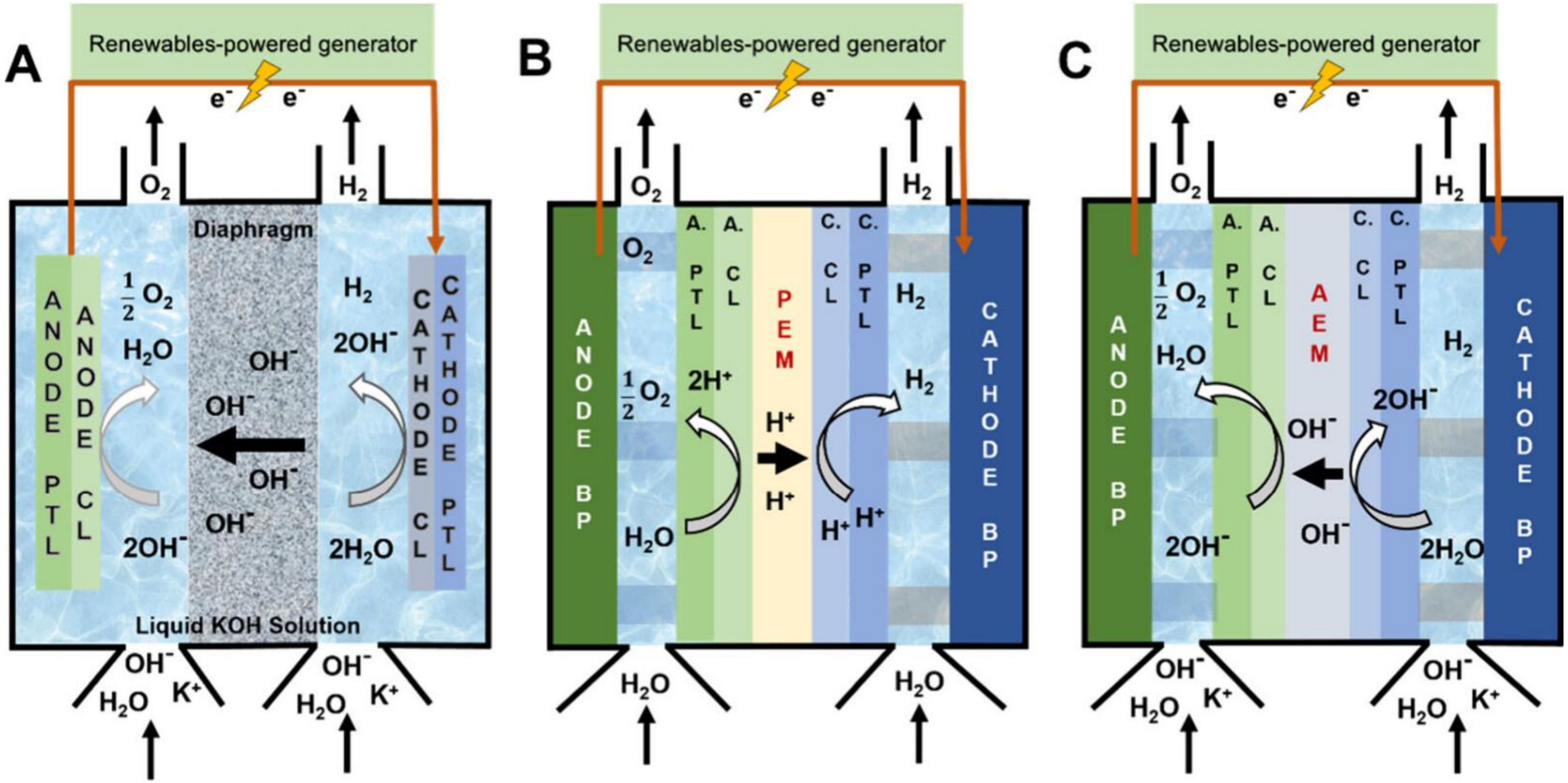
1800 Carlisle and Nicholson – used the Voltaic pile for electrolysis

1890 Charles Renard – water electrolysis for French military airships

1960s Proton Exchange embrane electrolysis at General Electric, military, and space applications, high costs
high-temperature electrolysis with solid oxide cells

1990s new interest in water electrolysis: H_2 as a green energy carrier for renewable energy sources

Electrolysis: A – alkaline electrolysis, B – PEM, C - AEM



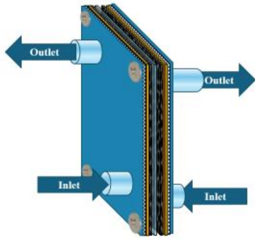
Reactions:
Anode: $2\ OH^- \leftrightarrow H_2O + 1/2\ O_2 + 2\ e^-$
Cathode: $2\ H_2O + 2\ e^- \leftrightarrow H_2 + 2\ OH^-$
Overall: $H_2O \leftrightarrow H_2 + 1/2\ O_2$

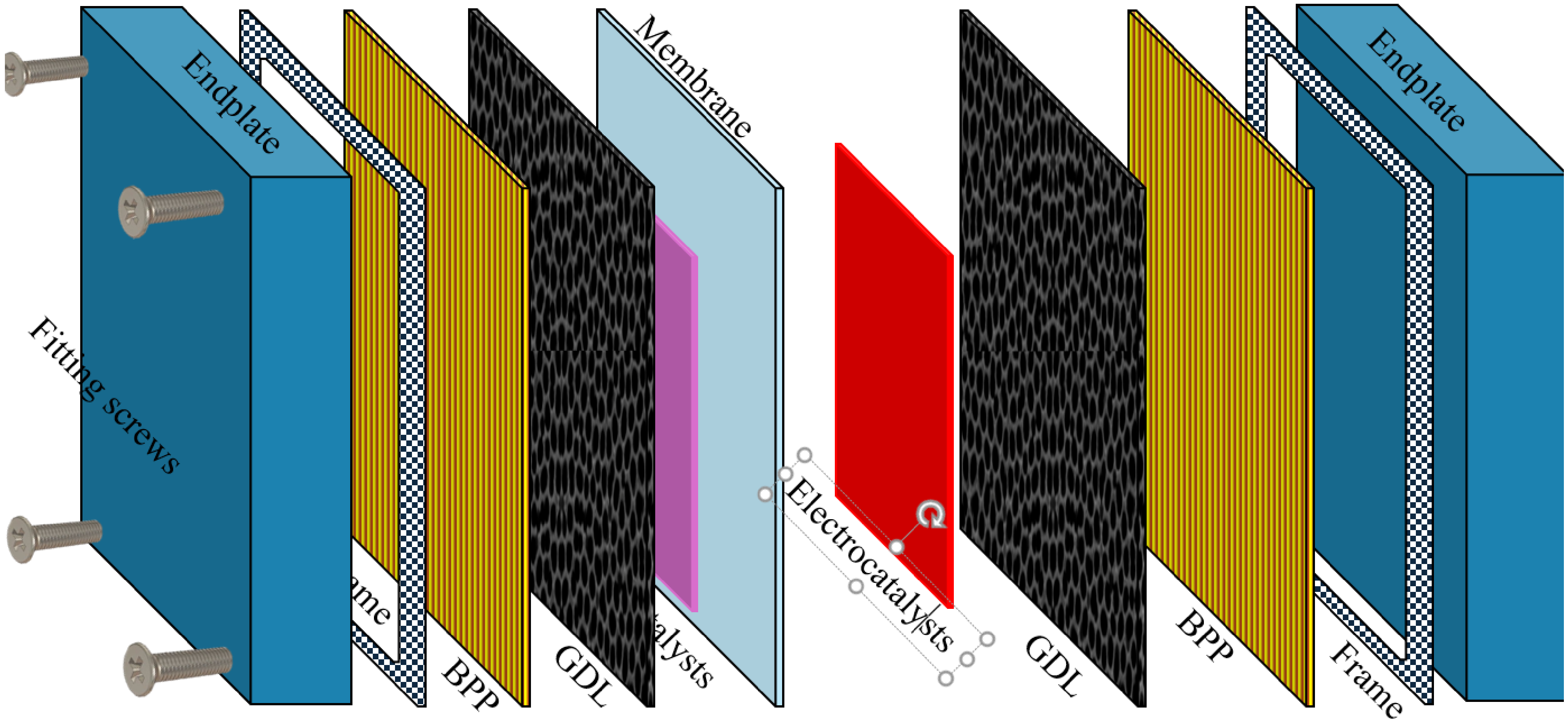
Reactions:
Anode: $H_2O \leftrightarrow 1/2\ O_2 + 2\ H^+ + 2\ e^-$
Cathode: $2H^+ + 2\ e^- \leftrightarrow H_2$
Overall: $H_2O \leftrightarrow 1/2\ O_2 + H_2$

Reactions:
Anode: $2\ OH^- \leftrightarrow H_2O + 1/2\ O_2 + 2\ e^-$
Cathode: $2\ H_2O + 2\ e^- \leftrightarrow H_2 + 2\ OH^-$
Overall: $H_2O \leftrightarrow H_2 + 1/2\ O_2$

	Alkaline Water electrolysis	PEM Water Electrolysis	AEM Water Electrolysis
Electrolytes	Aqueous KOH (25–40 wt%)	Proton exchange ionomer	Anion exchange ionomer
Cathode	Ni, Ni-Mo alloys	Pt, Pt-Pd	Ni & Ni alloys
Anode	Ni, Ni-Co alloys	RuO_2, IrO_2	Ni, Fe, Co oxides
Half-cell separation	Diaphragm (Zirfon Perl 500 µm)	Nafion 117 (e.g., 180 µm)	AEM (20–100 µm)
Operating temperature (℃)	65–100	50–90	50–80
Operating pressure (bar)	1-30	50-80	50-60
Current density (A cm^{-2})	0.2 – 0.4	0.6 – 2.0	0.2 – 1.0
Voltage (V)	1.8 – 2.4	1.8 – 2.2	1.8 – 2.2
Efficiency (%)	62 - 82	67 - 82	81 - 92
Gas purity (vol%)	>99.5	>99.9999	>99.99
Technology status	Mature	Commercial	R&D

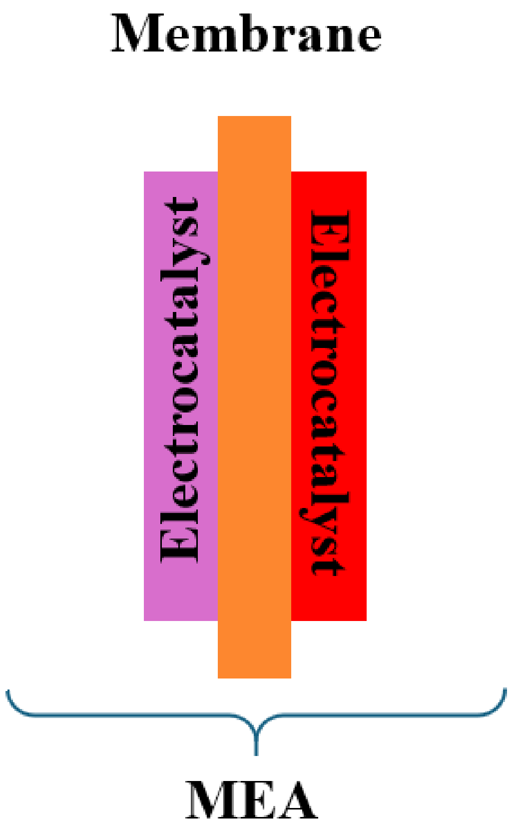
Electrolytic cell

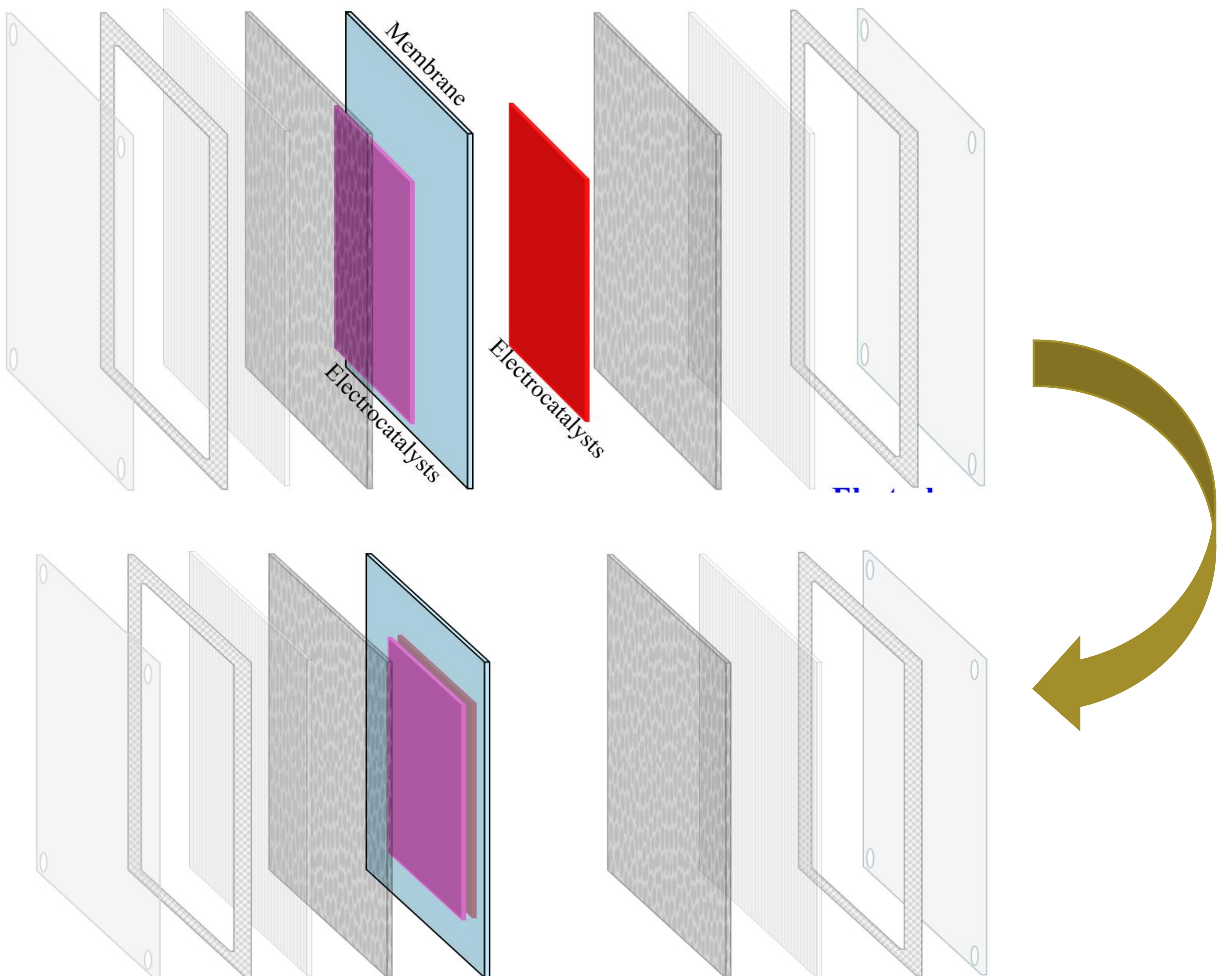




Author: Dr. Hanuman Thorat

MEA – Membrane Electrode Assembly

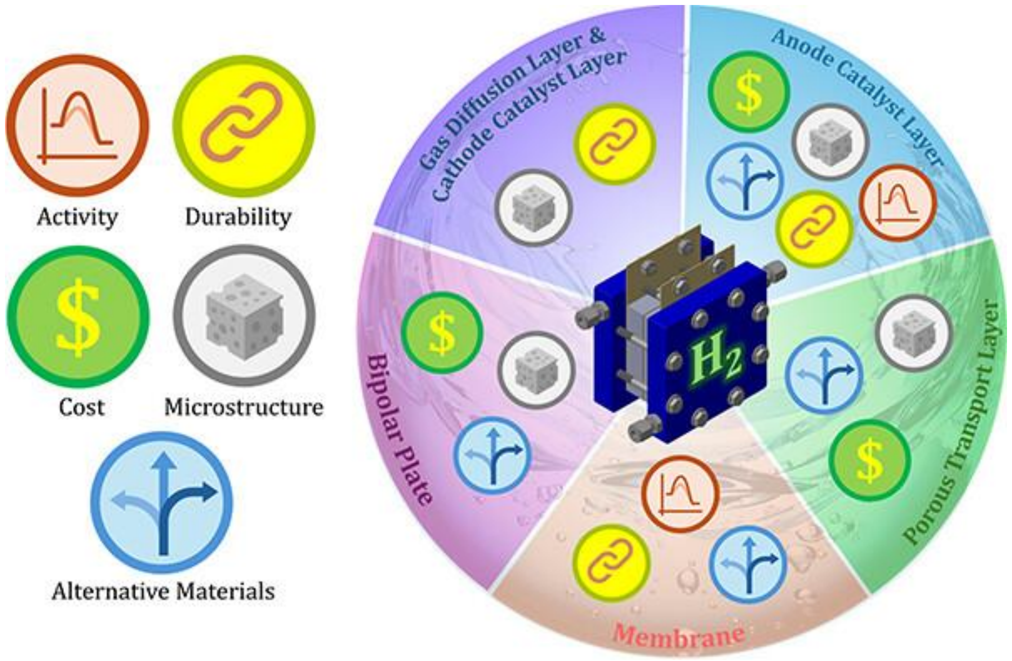




Desired properties of water electrolyzer system

- **High durability:** Ensuring components maintain consistent functionality over a prolonged duration.
- **High performance - hydrogen production rates and electrical efficiency:** High rates (current) over a small footprint.
- **Low capital expenditure:** preferential use of abundant and cheap materials, scalable synthesis of functional materials.
- **Ability to electrochemically pressurize hydrogen:** Pressurized H_2 is needed for transportation applications and reducing the reliance on external compressors brings energy savings.
- **Scalability**

Component Improvements



Chem. Rev. 2025, 125, 3, 1257-1302

Gas Diffusion Layers (GDL), Porous Transport Layer (PTL)

porous transport layers quickly delivering gas and water,
Anode: water to the catalyst layer, oxygen diffuses in the opposite direction
Cathode: water and hydrogen from membrane

Bipolar Plates (BP)

40 -60 % of the total cost of WE stacks
degradation – corrosive environment, surface protection

Optimization: mass transport and flow field structure - water flow, gas export, heat, and electron transfer, new materials

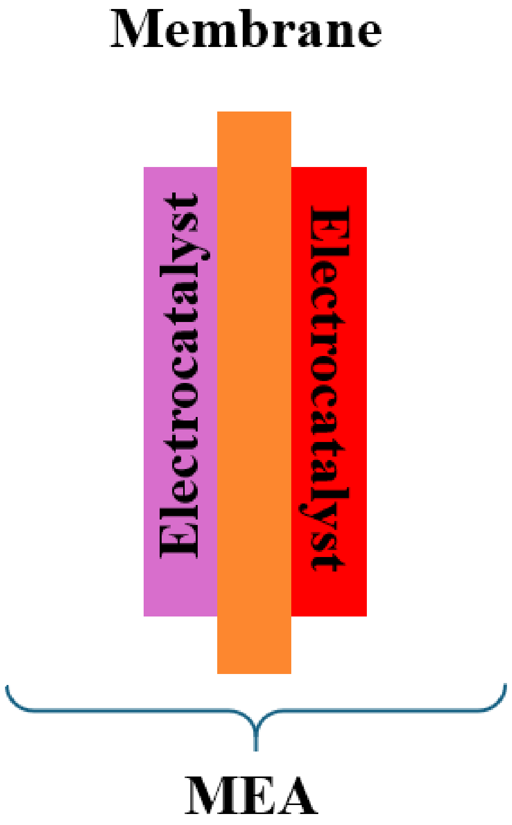
Ion exchange membrane (PEM, AEM)

Membrane electrode assembly

Membrane – critical component

Difference: PEM, AEM, AE, SOE etc.

Material: cationic or anionic polymers, Zirfon – polysulfone and zirkonia, solid ceramic membrane (600 – 900 °C)

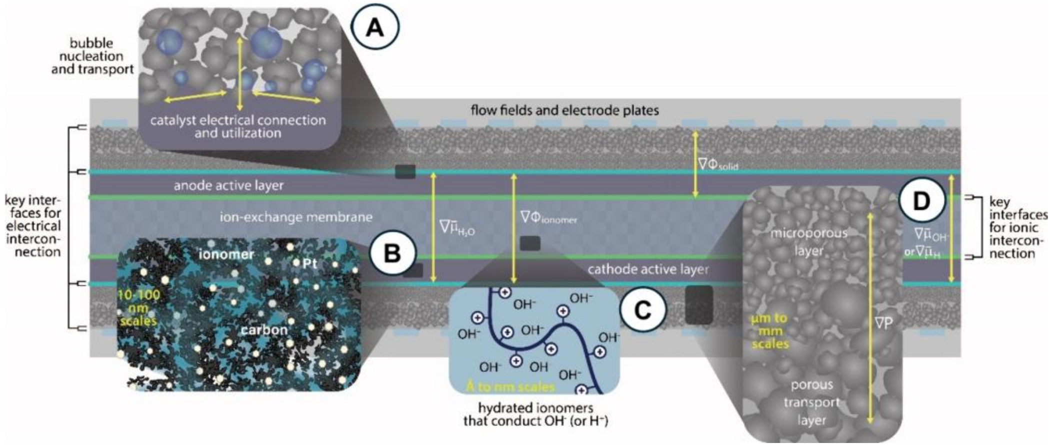


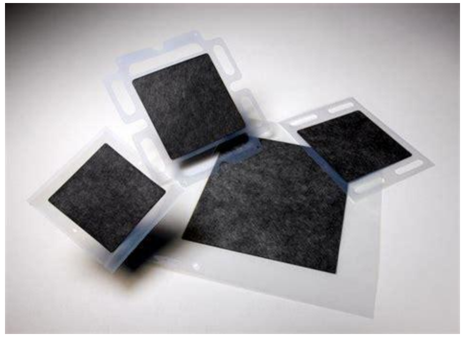
Catalytic layer

Catalyst-coated membrane (CCM)

Catalyst-coated substrate (CCS)

A combination of CCS for one electrode and CCM for the other (CCS/CCM)





(A) catalyst electrical connection and utilization; (B) C/Pt interaction with the ionomer; (C) hydroxide transport within the AEM; (D) pressure gradient within the catalytic layer, Chem. Rev. 2025, 125, 15, 6906–6976

PEM membranes

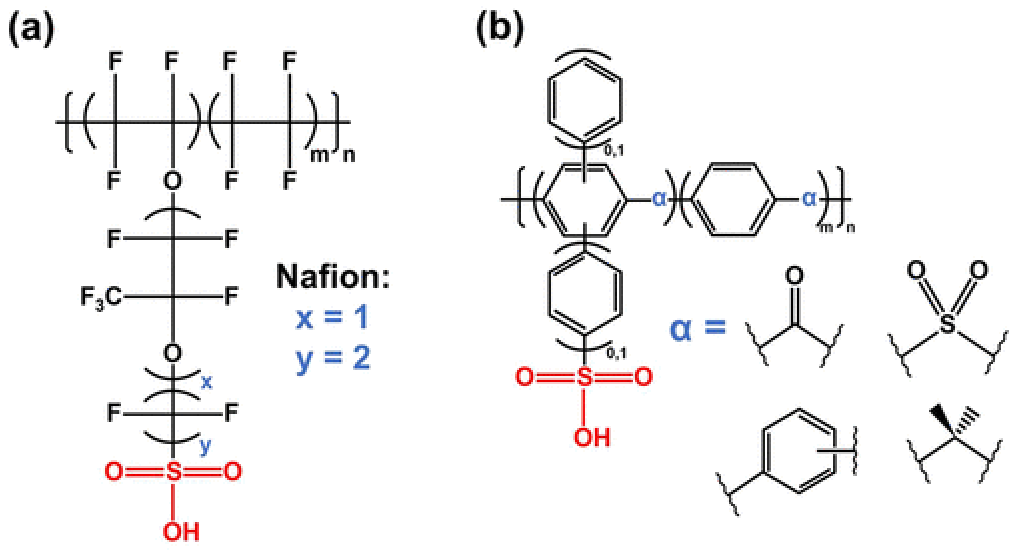
Perfluorosulfonic acid (PFSA), sulfonated aromatic hydrocarbons
anionic groups, hydrophilic side chains, hydrophobic backbone = cation conducting water channels

Proton conduction
Preventing gas crossover – H_2 and O_2 separation

- **operate in high current densities**
- **operate under dynamic electrical loads**
- **achieve high energy efficiencies**
- **produce high purity hydrogen (up to 99.999%)**
- **achieve long lifetimes**

Disadvantage
e.g. elevated ohmic overpotentials due to their high resistance to proton transport

Challenge:
More conductive polymer, reduced membrane thickness



(a) PFSA-based: a hydrophobic tetrafluoroethylene backbone with a hydrophilic side chain ending with a sulfonic acid group.
(b) Hydrocarbon-based: a network of rigid hydrophobic aromatic groups with sulfonic acid groups attached at some ends.

Membrane-Related Targets for PEMWEs (80°C, 30 bar Differential Pressure)

Parameter	units	current status (Nafion N115)	2026 target
Lifetime	h	60,000	80,000
Degradation Rate	%/1000 h	25	13
Activity @ 3 $A \cdot cm^{-2}$	V	2.0	1.8
PEM Thickness	µm	125	50
PEM Resistance	$m\Omega \cdot cm^{-2}$	100	30
H_2 Crossover	% H_2 in O_2	2	0.5

The conductivity of a PFSA ionomer is a strong function of its equivalent weight (EW), defined as the mass of polymer per mole of sulfonic acid (g/mol). N115 the highest conductivity.
Hydrogen gas crossover from the cathode to anode can lead to the formation of explosive mixtures as the lower explosive limit (LEL) of hydrogen in oxygen is just 4% (by volume). The problem occurs also with higher operational pressure.
Strategies: Three main strategies can be employed to mitigate gas crossover: 1) improving membrane gas-barrier properties, 2) implementing a recombination catalyst to react crossover hydrogen with oxygen (which forms water).

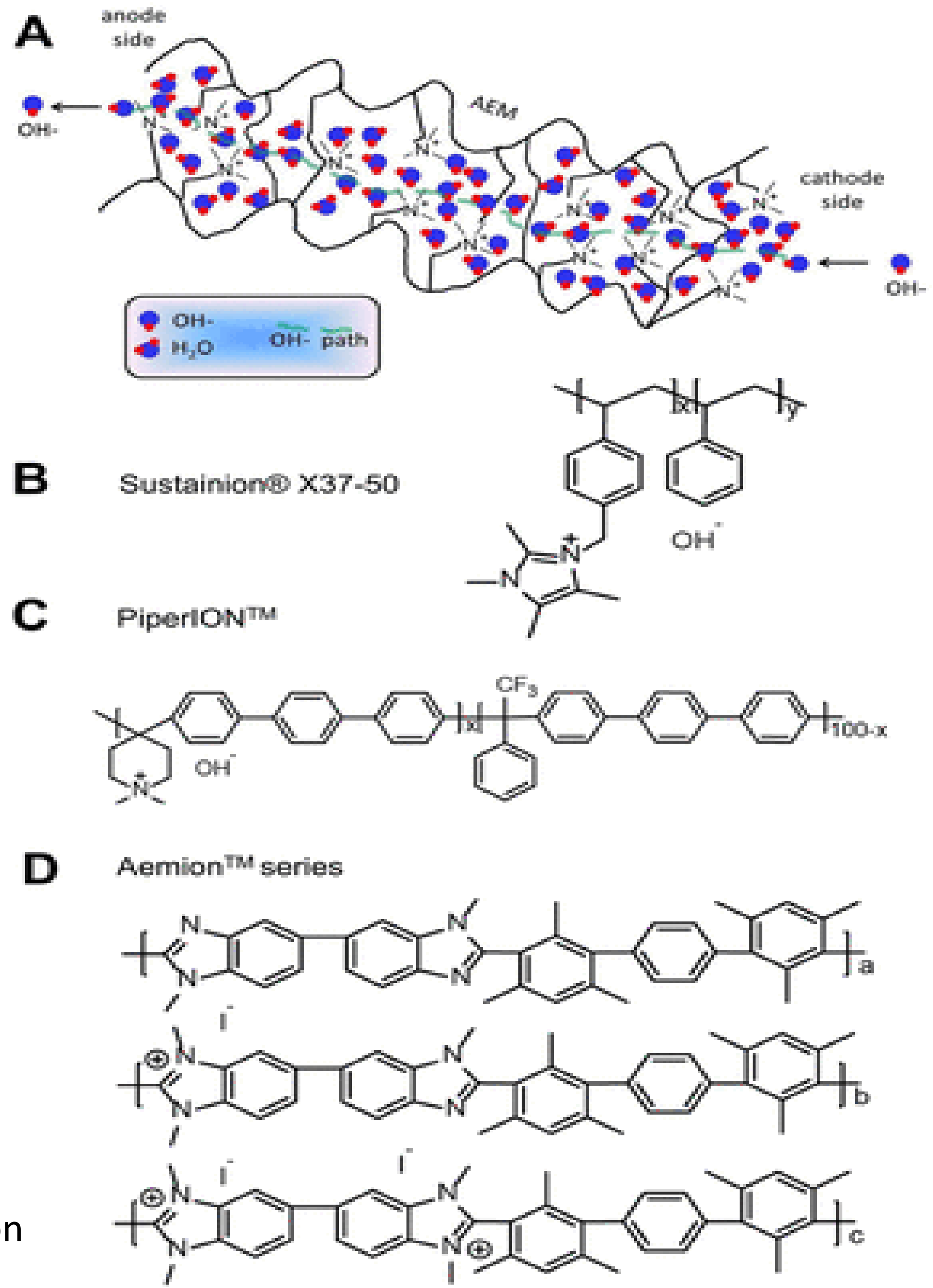
AEM membranes

Polymer backbone with cationic anchoring groups
providing anion conductivity and selectivity
hydrocarbon polymeric backbone:
Polysulfone, polystyrene to connect divinylbenzene, polybenzimidazol
specific anion exchange groups

Transport of OH^- groups to anode
Prevention of gas crossover

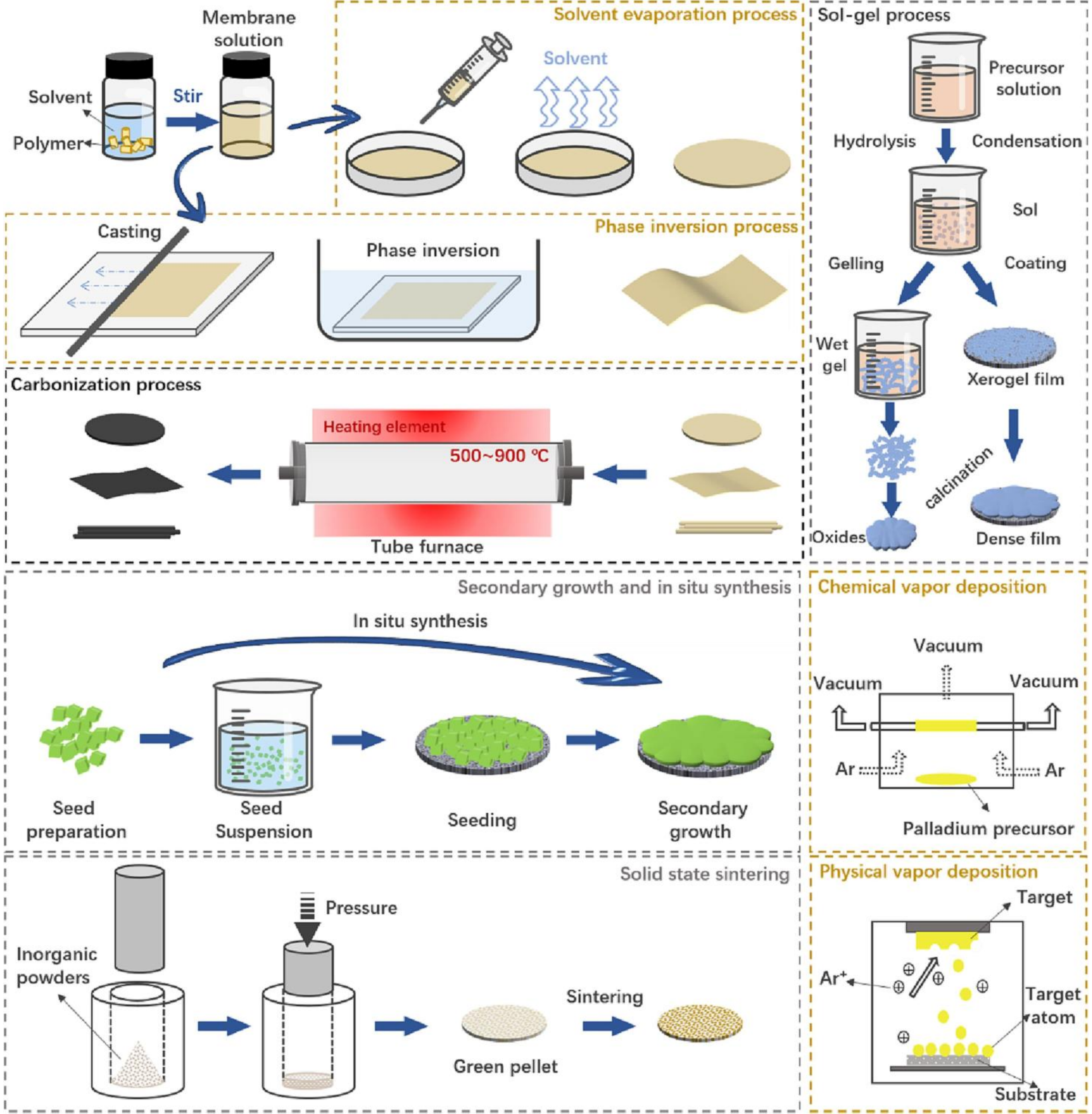
Low ionic conductivity and chemical stability (worse than PEM)
AEM membranes with the same thickness achieve considerable voltage losses from ionic conduction compared to PEM-WE when no OH^--containing supporting electrolyte is used.

An ideal AEM has a careful balance between moderate IEC and high MW to ensure effective operation in pure water-fed conditions



AEM based on a quaternary ammonium pendant functionl group (A), Chemical structures of Sustainion X37-50 (B), PiperION (C) and Aemion series (D). Chem. Rev. 2025, 125, 15, 6906–6976

General fabrication processes for different H_2-separation membranes.

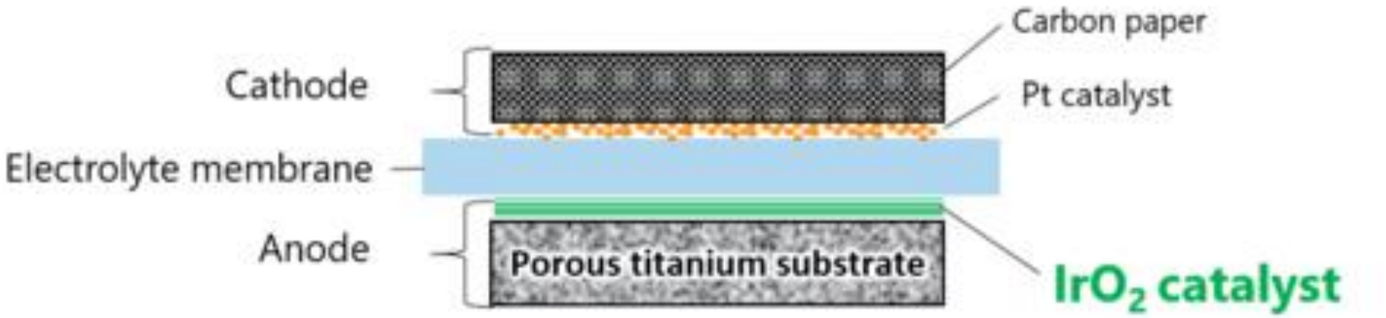


https://doi.org/10.1016/j.cej.2023.144328

Catalytic layers - Electrocatalysts

Key components of electrolyzers reducing the kinetic overpotentials for the HER and OER

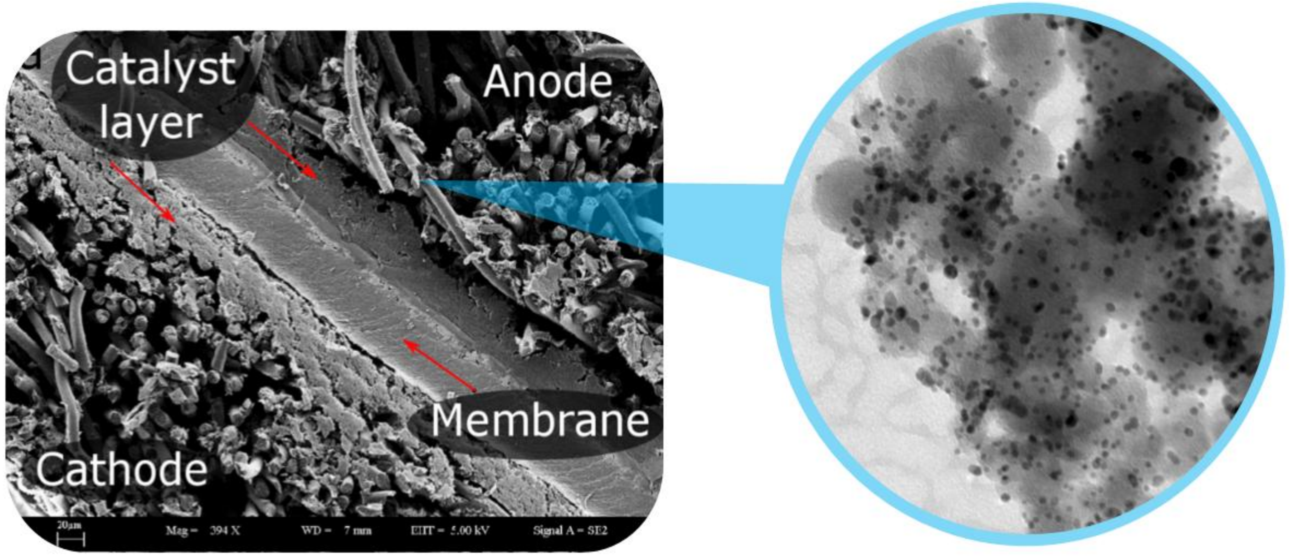
HER hydrogen evolution reaction (reduction)
OER oxygen evolution reaction (oxidation)



Activity

- **increasing the number of active surface site**
- **increasing the catalyst’s intrinsic activity**
- **increasing the electrochemical surface area**
- **form an electronically conductive network**
- **not to prevent the flow of species**

Stability
Cost-effective



- a catalyst is dispersed in an ionomer network on membrane or on PTL

Metal oxides

Layered hydroxides, spinels, perovskites – low conductivity
Pristine metal oxides – Ir, Ru, Ni, Co, WO_3. Mn_3O_4
Spinel-structured oxides – AB_2O_4 (Ni, Cu, Co, Fe)
Doped and mixed metal oxides – M-doped Co_3O_4, I-H_xWO_3

Metal phosphides and phosphates

Fe, Co, Ni,
CoP on Ti_3C_2/Mxene, Ni/RuP, transitionn metal phosphates

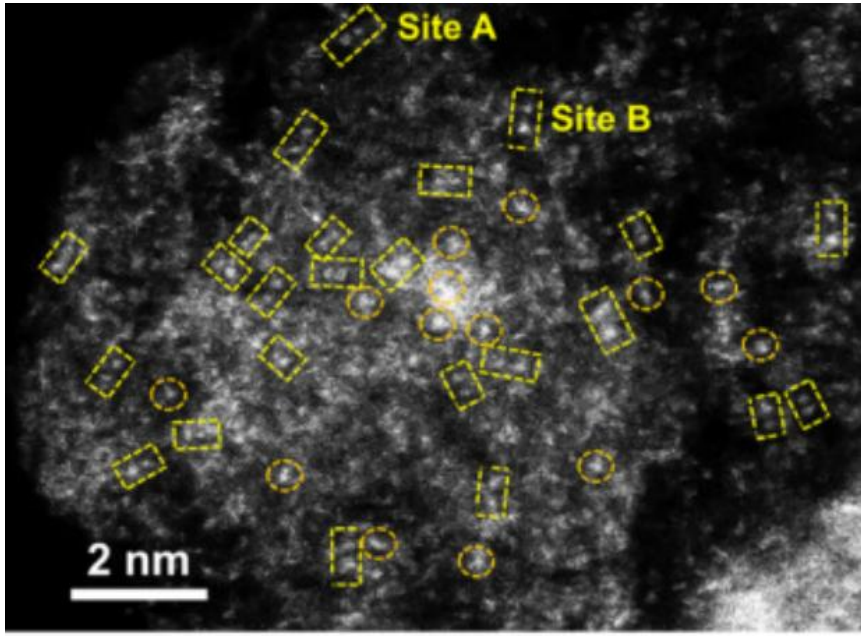
Metal nitrides, sulfides, selenides

Mo_3N_2, Co-(NiFe) nitride/oxide

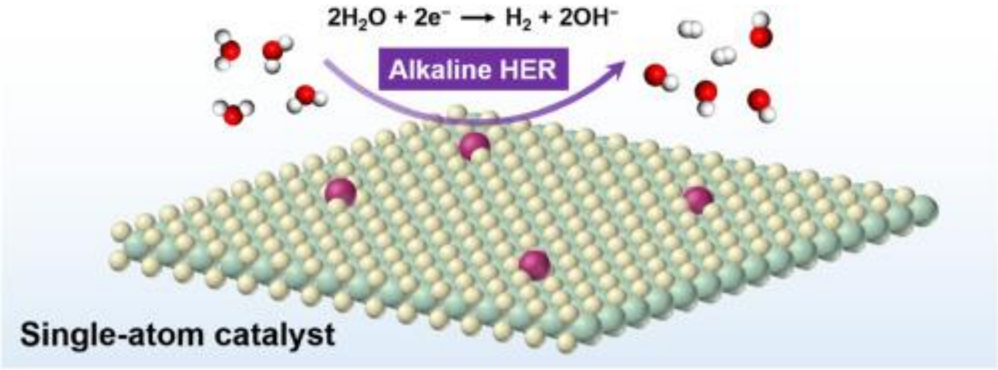
Carbon composites

CNTs, rGO, modified g-C_3N_4

Single atom catalysts

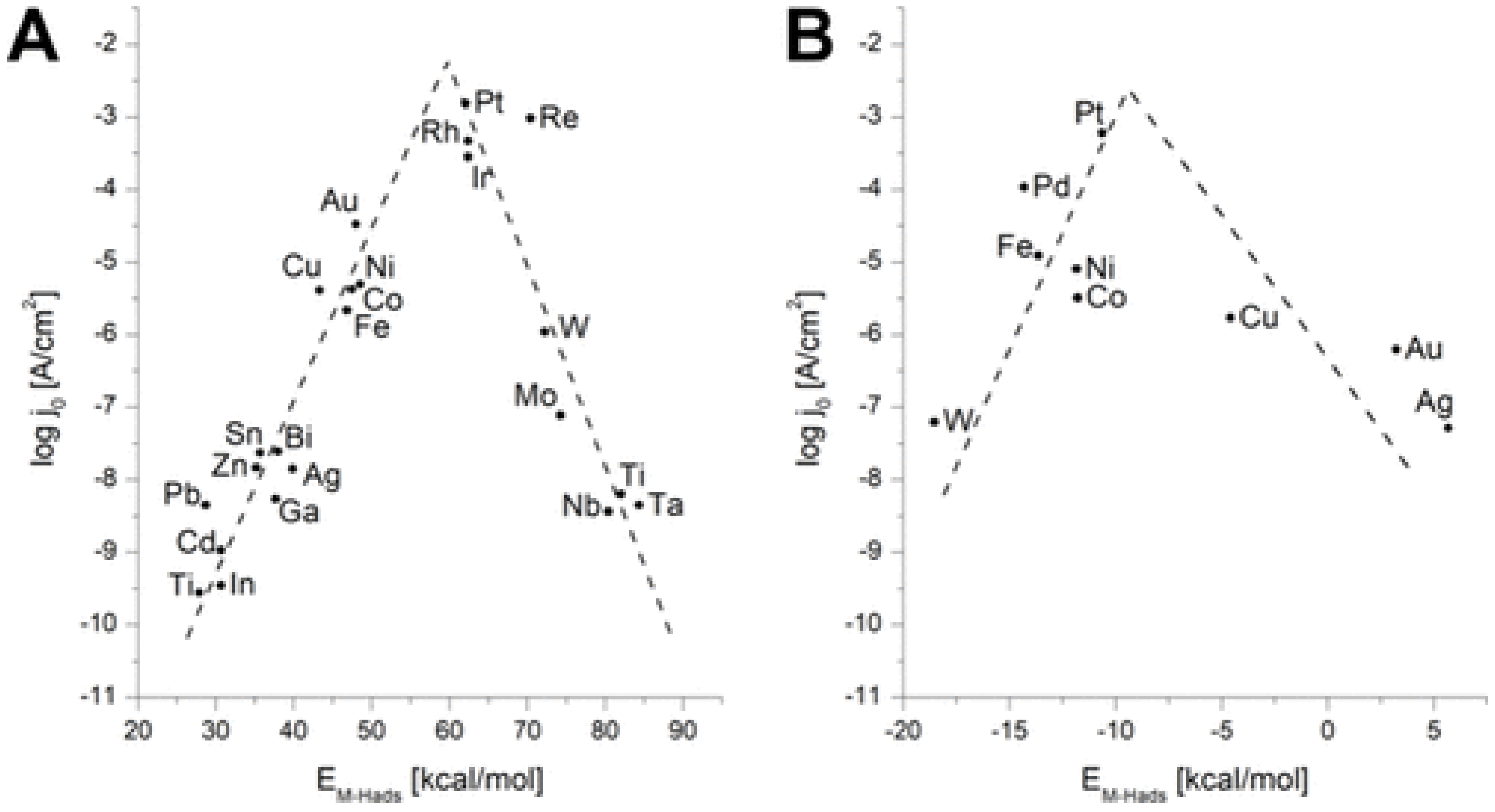


Aberration-corrected HAADF-STEM image of NiCo-SAD-NC. Yellow squares indicate the dimer sites while orange circles indicate the single Ni/Co atom sites.



https://doi.org/10.1016/j.matre.2022.100144

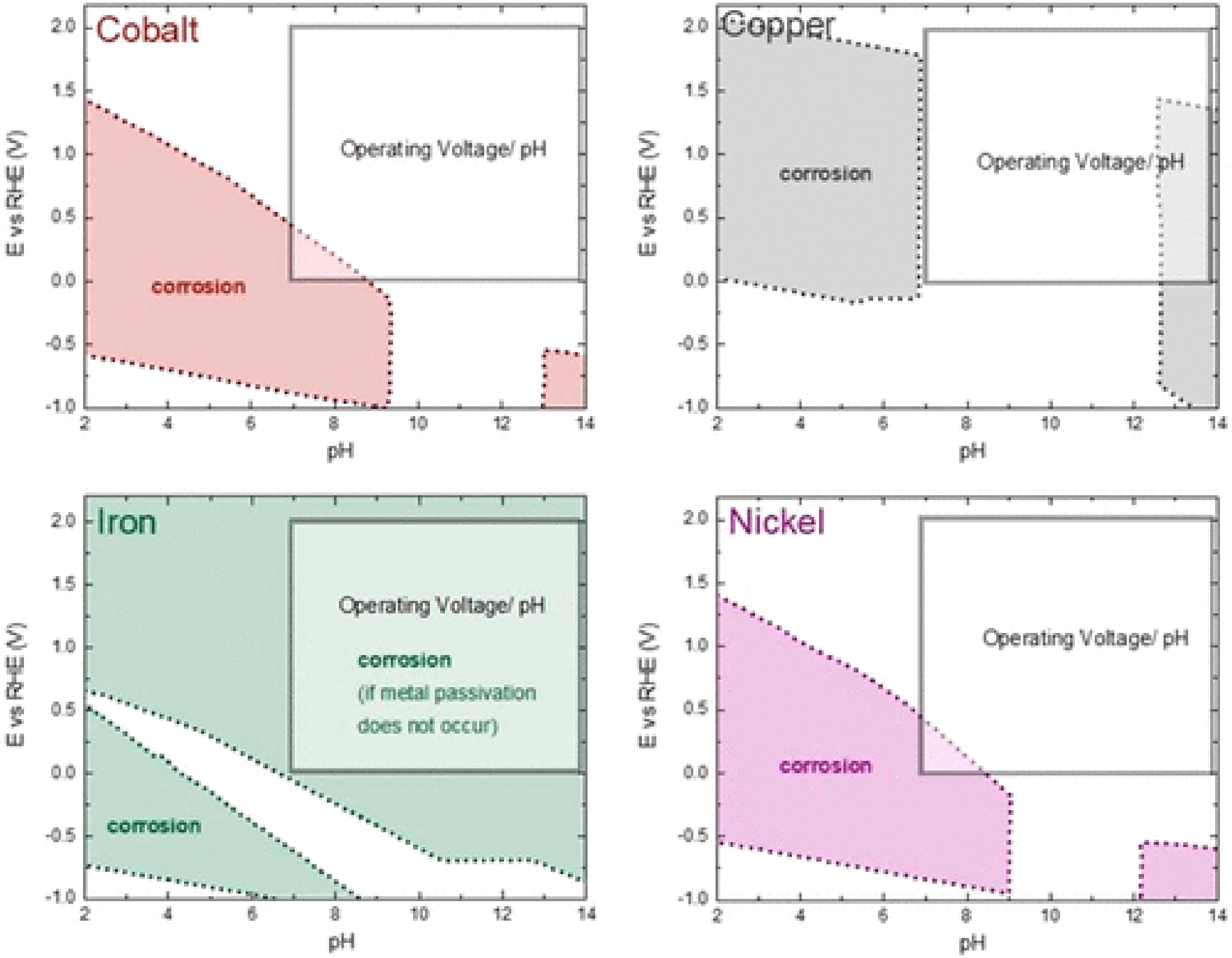
Volcano plots



Volcano plots of several transition metals for HER in (A) acidic and (B) alkaline conditions. In (A), EM-Hads is an experimental value, an operative electrochemical adsorption heat. In (B), EM-Hads was calculated using DFT.

Chem. Rev. 2025, 125, 15, 6906–6976

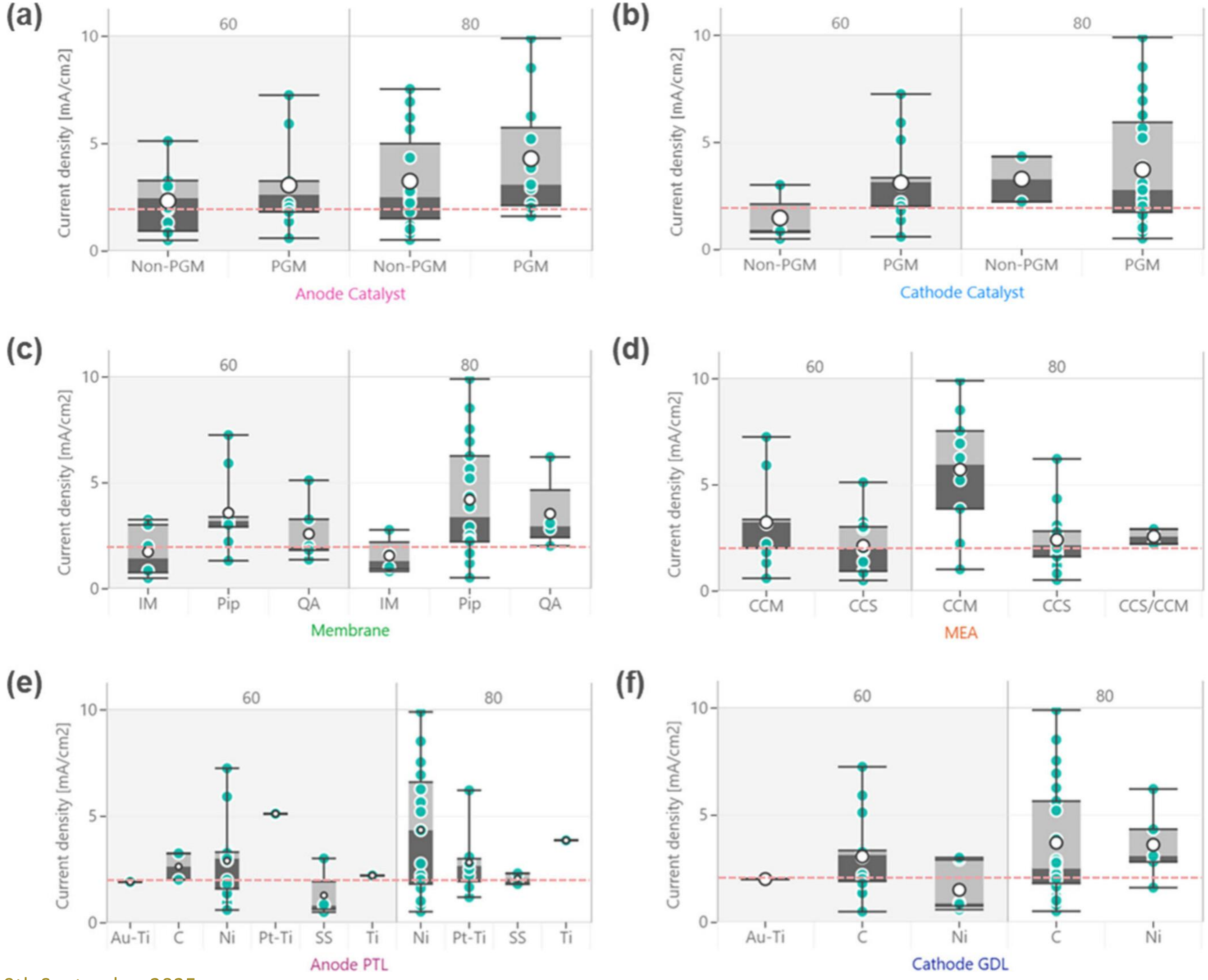
Pourbaix diagrams of cobalt, copper, iron, and nickel in aqueous electrolytes at ambient pressure and 25 °C. The inset shows the voltage–pH range.



Chem. Rev. 2022, 122, 13, 11830−11895

Impact of six key cell parameters on AEMWE performance at 1.8 V at temperatures of 60 and 80 °C

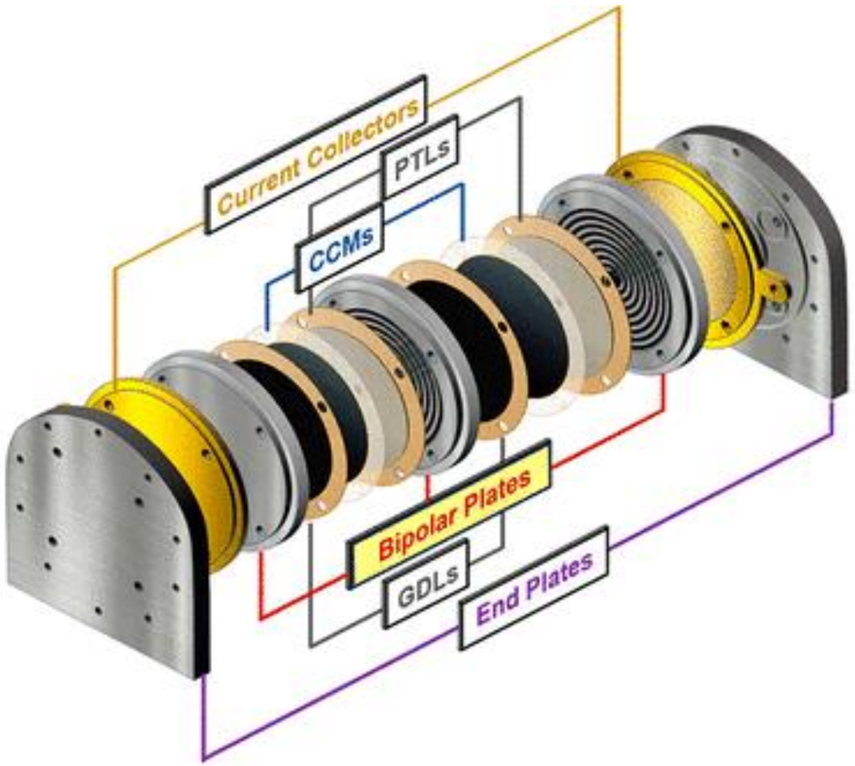
(a) anode catalyst,
(b) cathode catalyst,
(c) membrane,
(d) MEA configuration
(e) anode PTL,
(f) cathode GDL.
The red dashed line represents 2 A/cm² at 1.8 V.



ACS Energy Lett. 2025, 10, 7, 3058−3063

Conclusion - Outstanding research challenges

- **the design of efficient catalysts to minimize the overpotential and improve the energy efficiencies**
- **the development of non-noble metal OER electrocatalysts with high activity and long-term stability performance**
- **there is a limited knowledge of the detailed catalytic mechanisms especially for transition-metal-based HER and OER electrocatalysts.**
- **more effective electrocatalysts screening strategies are needed to establish the standard evaluation protocol for effective comparisons of the performances of catalysts from different research groups.**
- **the study of the impact of impurities**
- **degradation phenomena**
- **optimum catalysts loading**
- **membrane–composite membranes**
- **clean energy sources**



Thank you for your attention

Daniela Plachá
ERC, CEET, VŠB-TUO
Tel.: +420 608 828 829
Email: daniela.placha@vsb.cz