Cell-Level Challenges in Alkaline Water Electrolysers

Advanced Liquid Alkaline Water Electrolysis Workshop

January 26th, 2022

Ed Revers
R&D / Energy Transition & Hydrogen – USA

Outline

1. **De Nora Introduction**
2. Market Motivation
3. Setting Perspective from the Chlor-Alkali process
4. Interface and Component Specific Challenges (from the literature)
    1. Electrodes
    2. Bipolar Plates to Current Collectors (Comparison with PEMWE)
    3. Diaphragms
    4. Generalized Integration Challenges

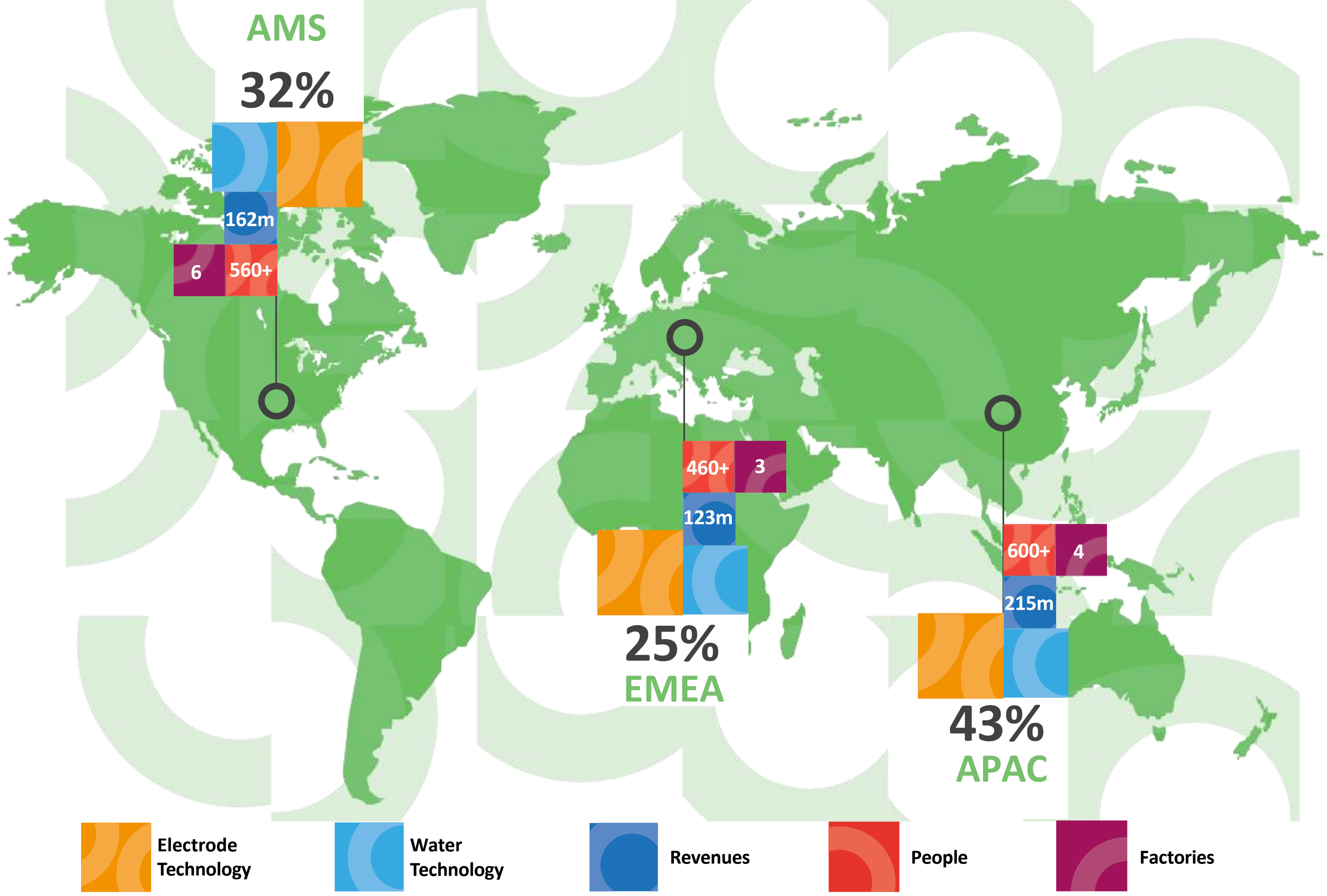
~300 Patent families

24 Locations

95+ Years of Innovation

€ 500m 2020 Revenues

1.600+ People



- Global reach complemented by local presence to better serve our customers
- Long-term relationships with our customers built on years of cooperation
- Largest installed base of insoluble electrodes & 10,000+ water systems worldwide
- Strong focus on innovation
- Well invested, state-of-the-art facilities, already optimized for future growth

Family owned Italian Company, founded in 1923, based in Milan

A legacy of successes thanks to technological breakthroughs that revolutionized modern electrochemistry.
A multinational group committed to innovation, targeting sustainable growth in clean energy and water thanks to continuous improvement.

DE NORA

FY2020

Since the foundation, Innovation in electrochemistry has been the driving force fueling De Nora's business growth

DE NORA

1965

Noble metal-coated titanium electrode patented *(Henri Beer)*

DSA® electrodes

1970

First application Chlorine Industry *Hg cells & Diaphragm cells*

Conversion of Nickel refining process

Hypochlorite *Onsite (sea water & brine) production cells*

Chlorine Membrane cells

1980

Salt chlorinators for *Swimming pools*

High speed electroplating *Electrodes*

1990

Copper Foil & Printed Circuit Board *Electrodes*

HCl electrolysis *Process*

2000

Advanced coating and separators for *chlor alkali*

2010

Water treatment *New coatings and systems*

Fuel Cells *Gas Diffusion Electrodes*

Green Hydrogen *New coatings*

2020

Green Hydrogen *Systems*

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MARKET: *H_2 colors and sources*

Hydrogen is a flexible and versatile energy vector that can be produced through several industrial processes

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Hydrogen production methods and colors:

Black	**Coal gasification** Reacting coal with oxygen and steam	***Current production methods***
Gray	**Natural Gas reforming** Reacting Methane and Steam (SMR)	
Brown	**Gasification** Fossil fuels gasification	
White	**By product of industrial processes**	
Yellow	**Electrolysis** Powered by the GRID	
Blue	**Black / Gray / Brown with Carbon Capture & Storage (CCS)**	**Low Carbon Hydrogen**
Green	**Electrolysis** Water electrolysis powered by Renewables	
Purple	**Electrolysis** Powered by nuclear energy	

Low Carbon Hydrogen processes:

Blue Hydrogen

COAL METHANE + STEAM REFORMING

\+

CO_2 MANAGEMENT (CCS – Carbon Capture and Storage)

Green Hydrogen

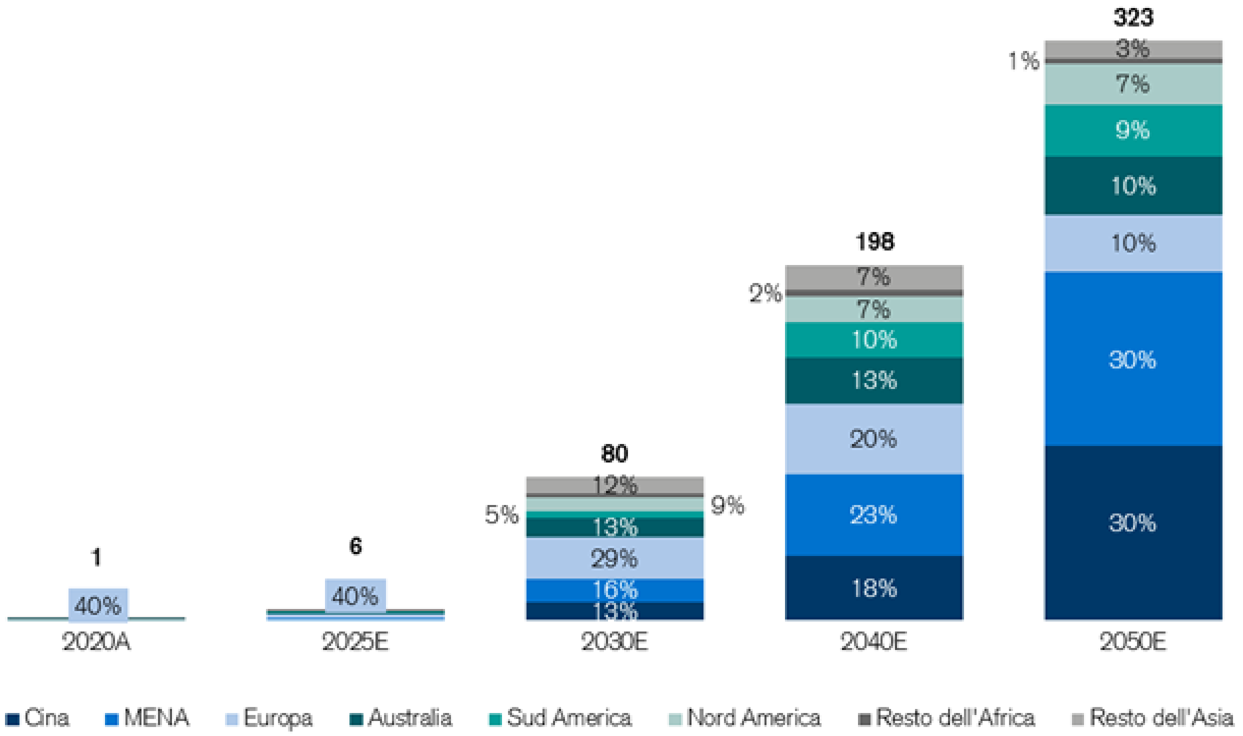
RENEWABLE ELECTRICITY + ELECTROLYSIS

Purple Hydrogen

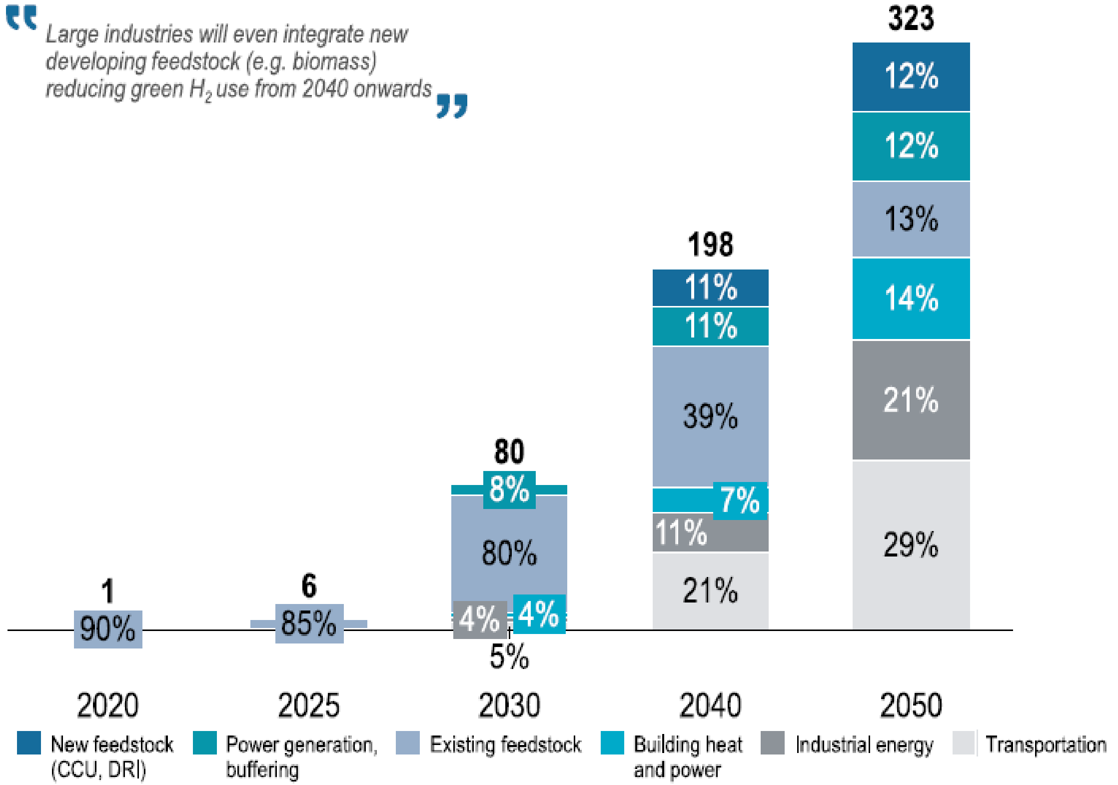
NUCLEAR ELECTRICITY + ELECTROLYSIS

Market Factors: *gH2 demand scenario*

Global green hydrogen production by geography (2020-2050; Mton)

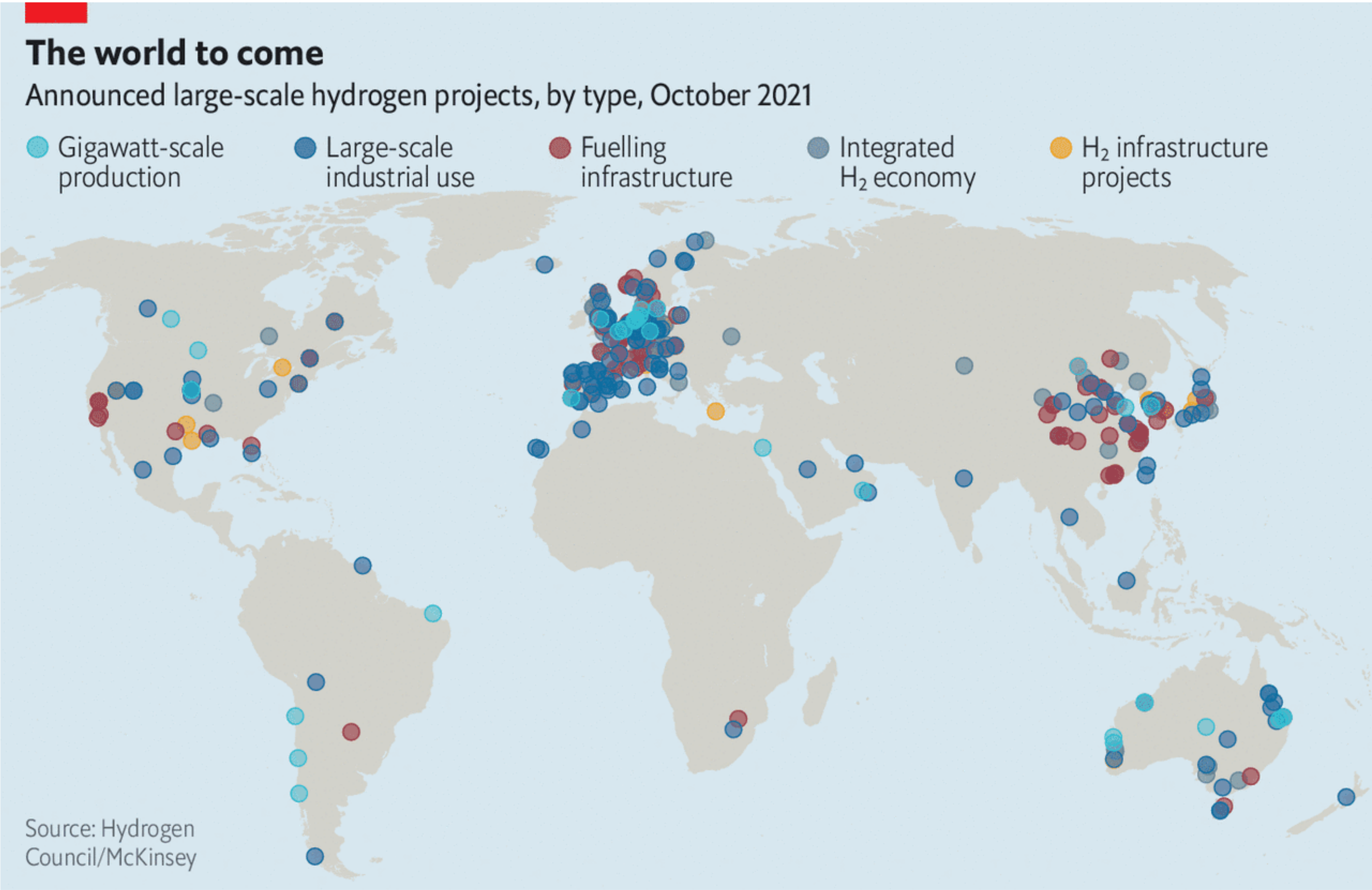


Global green hydrogen production by application (2020-2050; Mton)



Source: IEA, Aurora 202, Petrol Energy Outlook 2020, Expert Interviews, Hydrogen Council, Ronald Berger

Future Snapshot



The Economist

The target for LCOH, \$1/kg-H_2, is not only influenced by cell-level technology, but costs of renewables are also a key factor! Considering only the cell/stack, the roadmap must be to reduce PM, increase current density, while reducing footprint and number of cells!

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Historical Perspective – How the path to "Advanced Liquid AWE" is like Chlor-alkali

Chlor-alkali teaches us that a technology considered with little development prospects can make dramatic progresses.

Mixed Metal Oxide on Titanium invented by **Henri Beer*** in the 1960's

But before the development of **DSA® electrodes**, many other efficiency-improving electrodes were considered and dismissed for various reasons:

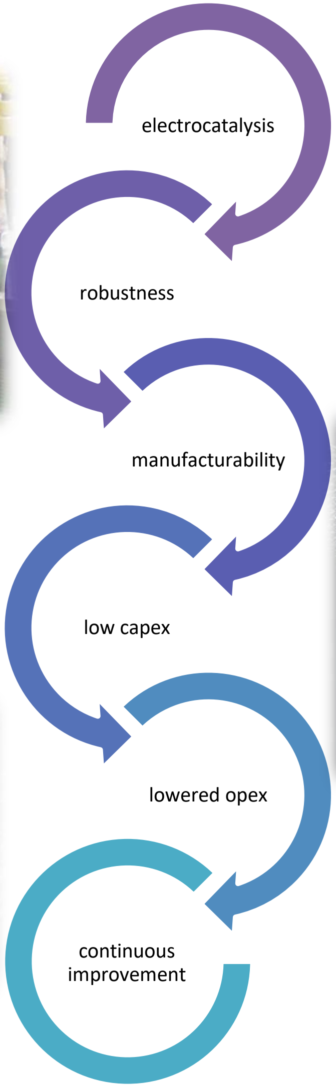
- *Solid platinum, retort carbon; Graphite; Magnetite, lead-silver, manganese dioxide; Platinum coated tantalum, niobium, zirconium*

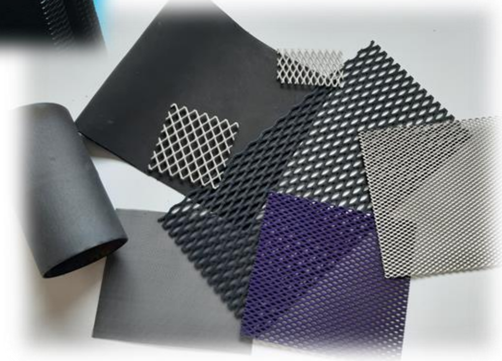
➢ DSA® electrodes all but perfected the Mercury Process, and enabled the evolution towards more energy-efficient Diaphragm and Membrane Processes

➢ **The step-changes, in process and materials, throughout the evolution of Chlor-alkali electrolysers show us a development pathway away from "Traditional Alkaline Water Electrolysers" to "Advanced Alkaline Water Electrolysers"**

*Key characteristics of the DSA® electrodes:
Self-protective, shape preserving (non-reactive), resistance to current reversals, manufacturability, coat-ability, advanced design enabling

Challenges that needed to be addressed in the realization of DSA®

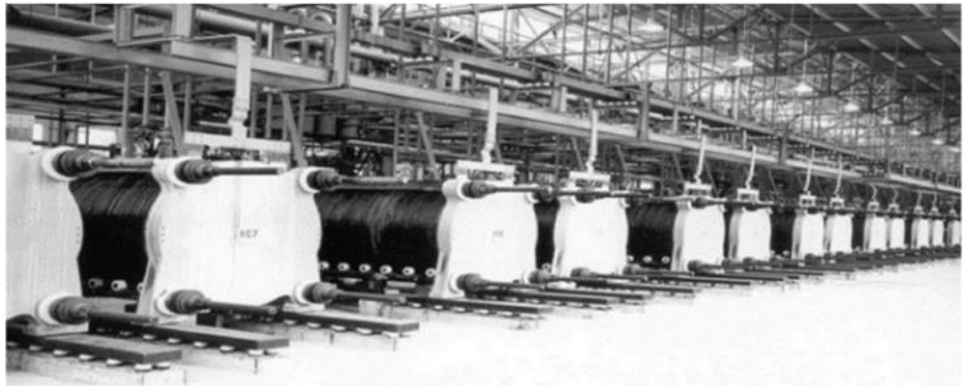




…from the lessons of the previous slide

Liquid Alkaline Water Electrolysis and the New State-of-the-Art (SoA)

Taken from Ayers et al. *Annu. Rev. Chem. Biomol. Eng.* (2019)



135 MW historic hydro-power electrolysis-based hydrogen production in [Glomfjord](), Norway 1953-1991

Parameter	Membrane Chlor/Alkali	Similarity (1=low,5=identical)	Advanced AWE
Reaction	2 H_2O + 2 e^- → H_2 + 2 OH^-	●●●●●	2 H_2O + 2 e^- → H_2 + 2 OH^-
Electrolyte composition	30-33% NaOH	●●●●	28-30% KOH
Electrolyte physical state	Liquid – Gas mixed phase	●●●●	Liquid – Gas mixed phase
Electrolyte Resistivity	~0.8 W* cm	●●● (less intense for AWE)	~0.6 W* cm
Electrolyte purity	HIGH	●●●●	HIGH
Current Density	5.0 – 8.0 kA/m2	●●●	8.0 - 12.0 kA/m2
Temperature	80 ÷ 90°C	●●●●	70 ÷ 90°C
Pressure	0.0 ÷ 0.5 bar(g)	●● (little influent)	10 ÷ 30 bar(g)
Cathode support	Light mesh nickel made	●●●●●	Light mesh nickel made
Mechanical setup	Zero gap with elastic mean	●●●●●	Zero gap with elastic mean
Reversal current shutdown(1)	YES	●●●	YES

Traditional Alkaline Water Electrolysis, realized at industrial scale since the early 1990s, **was** typically characterized as a finite-gap electrolyser. In this design, gases evolved between the electrodes and the separator, which led to limitations in operating current density (0.8 – 2.0 kA/m^2). **To advance from 'Traditional AWE' to 'Advanced AWE', we have realized:**

SoA ≠ "Traditional" Alkaline Water Electrolysis

SoA = "Advanced" Alkaline Water Electrolysis

SoA = ↑ Power Density (zero-gap, increased current density)

SoA = ↑ Efficiency (zero-gap, lowered OPEX)

SoA = ↑ Electrocatalysis (further lowered OPEX)

SoA = ↑ Pressurization (system level improvements)

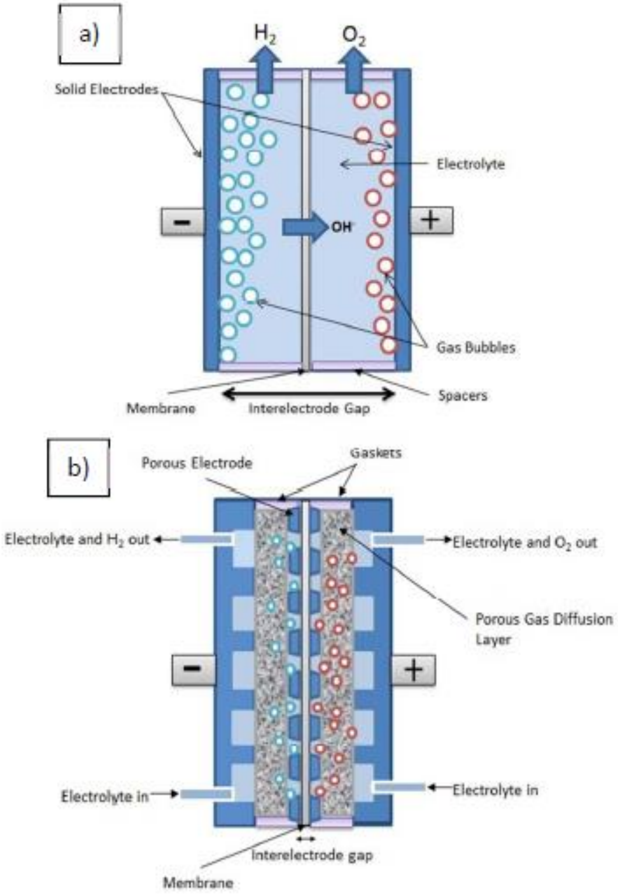
SoA = ↑ Material Advancements

Note: These improvements have been realized in the recent past and serve now as the foundation for Advanced AWE continuous development

- Nowadays, the experience derived from Chlor-Alkali was used as a starting point, **but it is not the end point**

Critical design change enable Advanced AWE

- Zero-Gap Technology is another key technology to further reduce **Specific Power Consumption**, kWh/Nm^3H_2)
- Cell Voltage is the sum of different components: thermodynamics, electrode kinetics (minus electrocatalytic coating contribution), ionic-ohmic loss, and structural-ohmic loss
- A **properly designed electrode components/package** minimizes ionic-ohmic and structural-ohmic losses
- **Zero Gap** removes the ionic-ohmic drop related to inter-electrodic gap: a significant **cell voltage reduction** is obtained!
  - In finite gap cells, there's space between the cathode and the diaphragm, a space representing an ohmic drop penalizing cell voltage
  - In zero gap cells, the electrodes are directly placed in contact with the diaphragm, usually with some force
    - An important distinction is made between "fixed zero-gap" cells and "dynamic zero-gap" cells

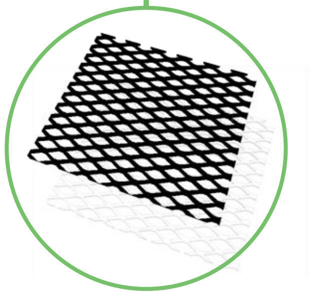


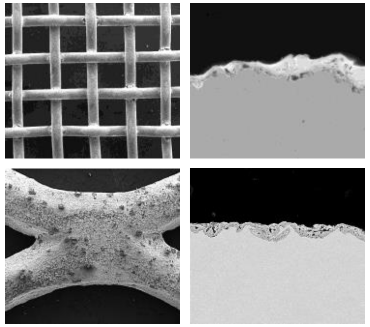
Different designs for alkaline electrolytic cells. Figure (a) shows a conventional cell design with a well-defined spacing between the electrodes, figure (b) shows the zero-gap design in which the electrodes are directly placed in contact

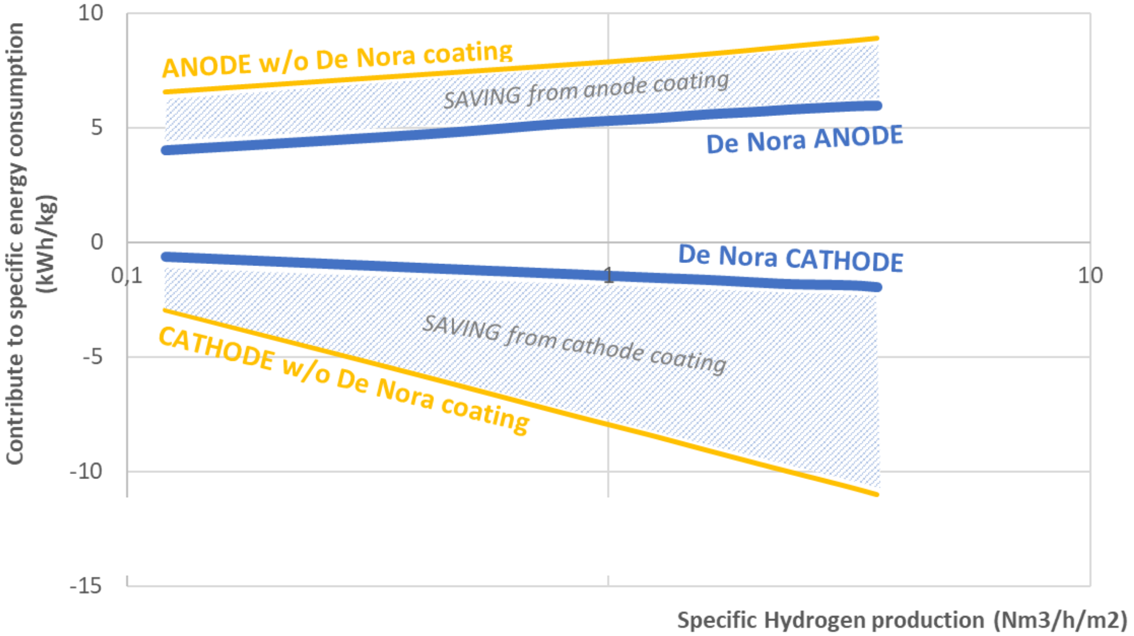
Motivation to improve upon existing electrode packages

Cost-efficient coatings will contribute greatly to the reduction of LCOH in all markets

Anode and cathode advanced electrodes are continue to make liquid-AWE more attractive







Items that must be addressed wholistically:

- Continue to push higher current density (already achieved >10 kA/m²), thus reducing CAPEX intensity and Stack Footprint
- Reduce Power Consumption through Lowering Cell Voltage
- Ensure Lifetime stability (integration with renewables)
- Use for Atmospheric & Pressurized Alkaline Water Electrolysis

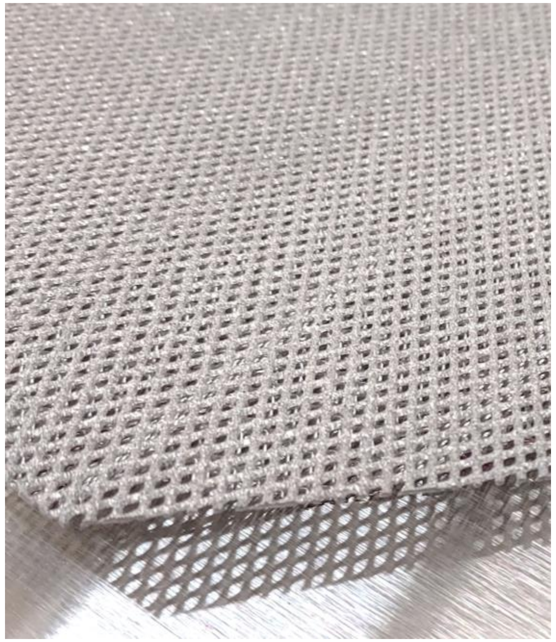
Advanced AWE is already available

World's first giga-scale green hydrogen electrolyser set for Saudi mega-city after Thyssenkrupp deal

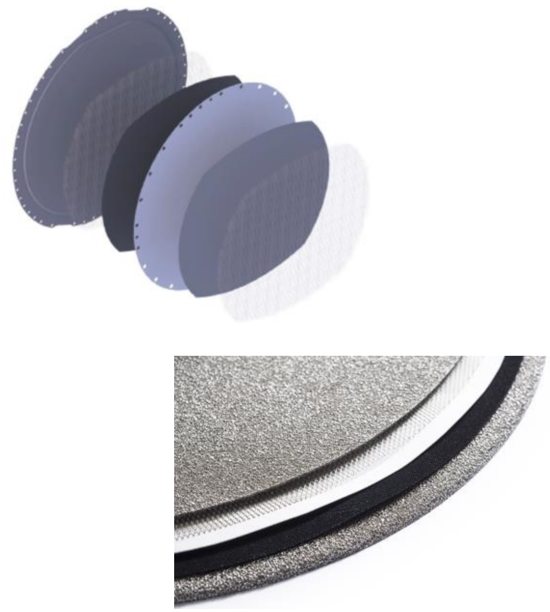
German industrial conglomerate Thyssenkrupp wins contract from Air Products for 2GW electrolysis plant at $500bn Neom future city showcase

December 12th, 2021: https://www.rechargenews.com/energy-transition/world-s-first-giga-scale-green-hydrogen-electrolyser-set-for-saudi-mega-city-after-thyssenkrupp-deal/2-1-1122277

Activated Electrodes



Other Zero-Gap Cell Components



- Advanced Electrodes and Catalytic Coatings are among the key components for Advanced Alkaline Water Electrolysis systems, and their integration into Zero Gap AWE designs being realized now. However, further improvements will need to be realized to match LOCH targets in a broader range of applications and regions.

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Challenges in designing electrodes for the continuous improvement Advanced AWE

Given the target (high) operating current density, low cell voltages, durability expectations, and other process conditions – electrodes should be designed as follows:

- High Catalytic Activity
- High Surface Area
- High Conductivity
- Reduced Bubble Effect
- High Permeability and Wettability

Consider an "activated" electrode, and challenges associated with the achieving optimal design:

- Stability (structural)
- Stability (chemical)
- Manufacturability!

Unfortunately, the lessons learned from IEM systems are not directly applicable to advanced liquid AWE systems. This becomes more obvious as other components are integrated within the design of the electrolysers, such as current collectors and bipolar plate interfaces. Here, the catalyst needs to be applied to MASSIVE metal substrates (vs polymer-binded catalyst).

Taken from Haverkort et al. *J. Power Sources* (2021)

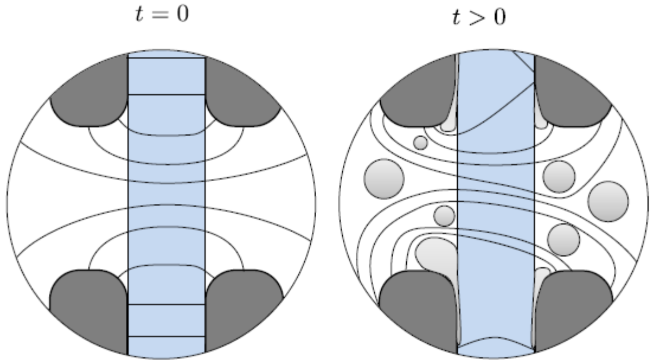


Fig. 1. An idealized schematic of possible low current density streamlines through the separator (light blue) between two electrodes (dark gray) at $t = 0$ immediately after the current is switched on and no bubbles (light gray) have yet formed (left) compared to some time later where the current lines have to go around the generated bubbles (right). Disclaimers: anode and cathode holes will not generally be this aligned; at higher current densities and in 3D the streamlines can stay closer to the separator; gas formation between the separator and diaphragm is speculative.

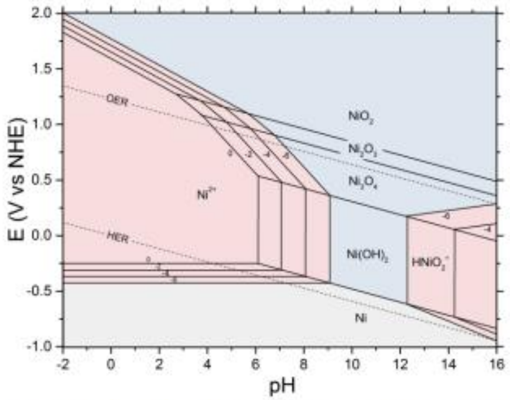


Figure 11. Pourbaix diagram of nickel, replotted using the equations reported in reference [114]. With reference to a concentration of dissolved Ni ions of 1 µM, the grayish area represents immunity against corrosion, the blueish area passivation and the reddish area dissolution.

Taken from Schalenbach et al. *Int. J. Electrochem. Sci* (2018)

A Classical Example from High Surface Area Nickel Electrodes

Raney, Raney-like, skeletal, sponge Nickel

How they are made impacts performance

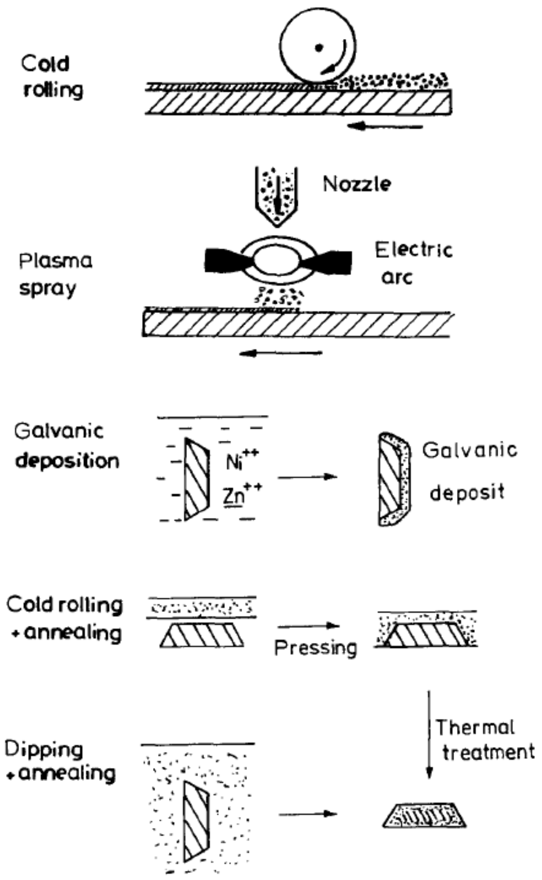
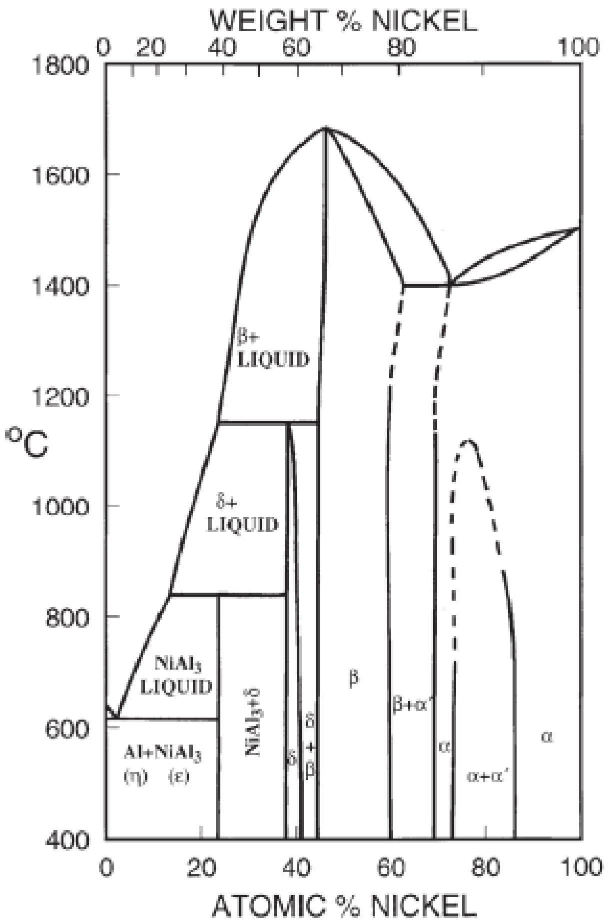


Fig. 1. Schematic presentation of several procedures for applying leachable Raney-nickel precursor alloys to the surface of supporting nickel or stainless steel cathodes.

Taken from Boruciński et al. *J. Applied Electrochemistry* (2012)



Taken from Fernández et al. *InTechOpen* (2012)

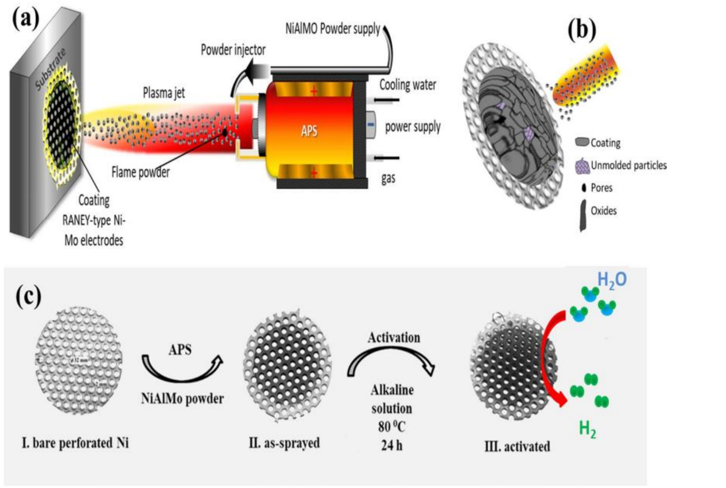
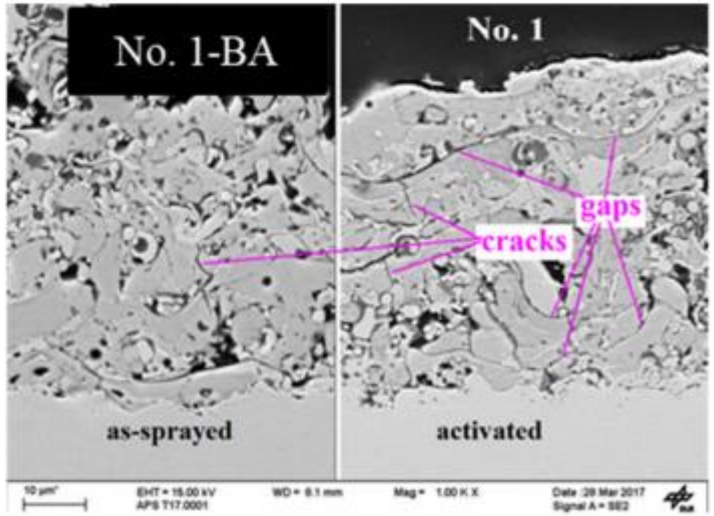


Figure 1. (**a**) Schematic illustration of APS coating of Raney-type Ni–Mo electrode on perforated nickel sheet. (**b**) Schematic structure of a thermal sprayed coating. (**c**) Coating process and chemical activation of Raney-type Ni–Mo electrodes.

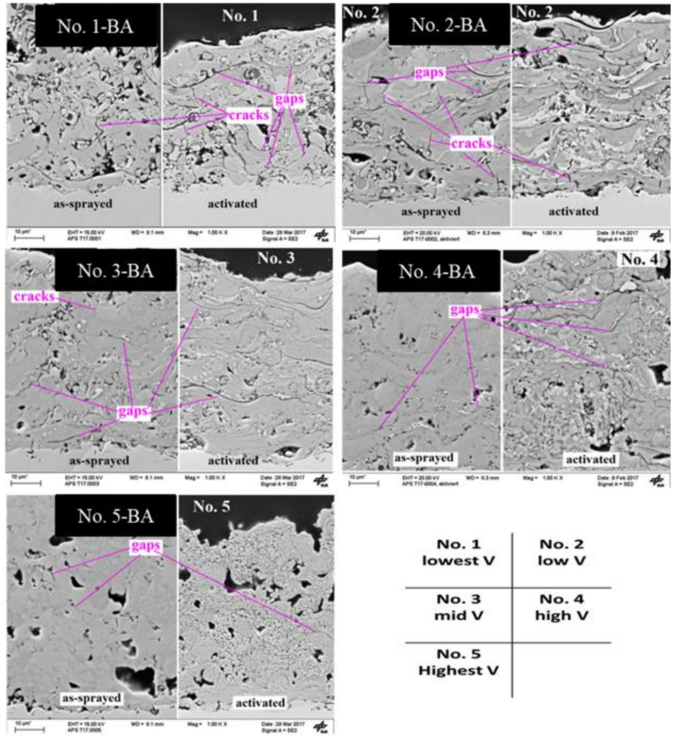


Taken from Razmjooei et al. *Scientific Reports* (2020)

Opportunities for further improvement in the development of “advanced electrodes”

- Advanced coated electrodes are still the key to unlocking robust, durable, and efficient electrolysers
- Variability in the production processes can impact measured performance of high surface area electrodes, considering the scale required for Green Hydrogen (millions of meters-squared of electrodes needed by 2030)
- The role of Nickel oxidation on activity throughout the expected lifetime of the electrodes (at the bulk and at the interfaces) may impact lifetime if not properly protected
- Coatings enhance drastically the cell efficiencies which will lead to realizing sustainable, non-noble metal catalysts
- On a system-level, controlling for electrolyte impurities (in the case of nickel-iron oxyhydroxides) remains important
  - Not only to guarantee high performance, but also to protect masking of the catalytic coatings

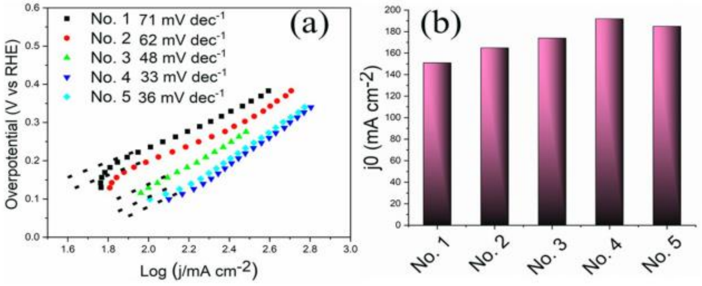
This just serves as a taste of the challenges that remain, especially considering that a **primary benefit of AWE is to reduce or eliminate the need for PGMs, as efficiency and power density increase for advanced alkaline water electrolysis, ultimately lowering the expected LCOH in every market.**

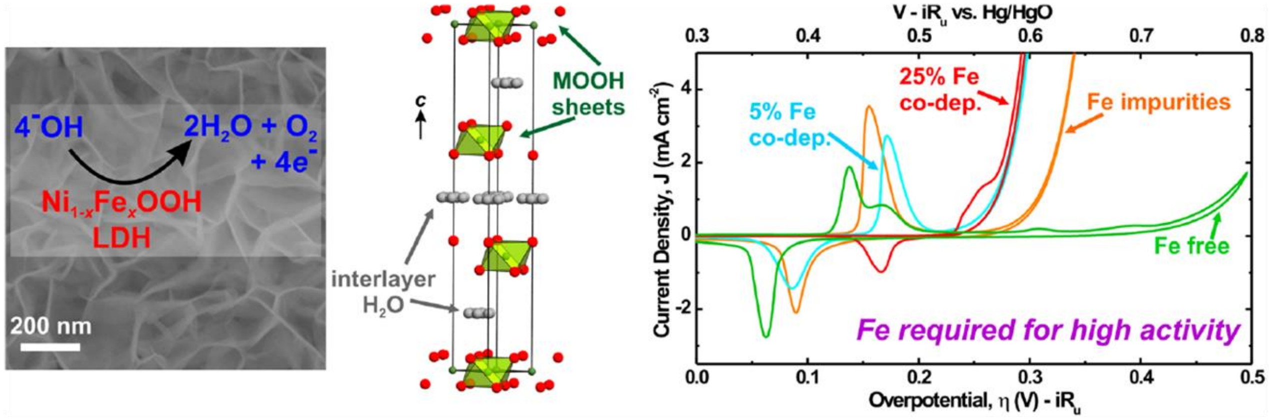


No. 1 lowest V	No. 2 low V
No. 3 mid V	No. 4 high V
No. 5 Highest V	

Figure 3. SEM images of all APS-based Raney-type Ni–Mo electrodes before and after activation.

Taken from Razmjooei et al. *Scientific Reports* (2020)





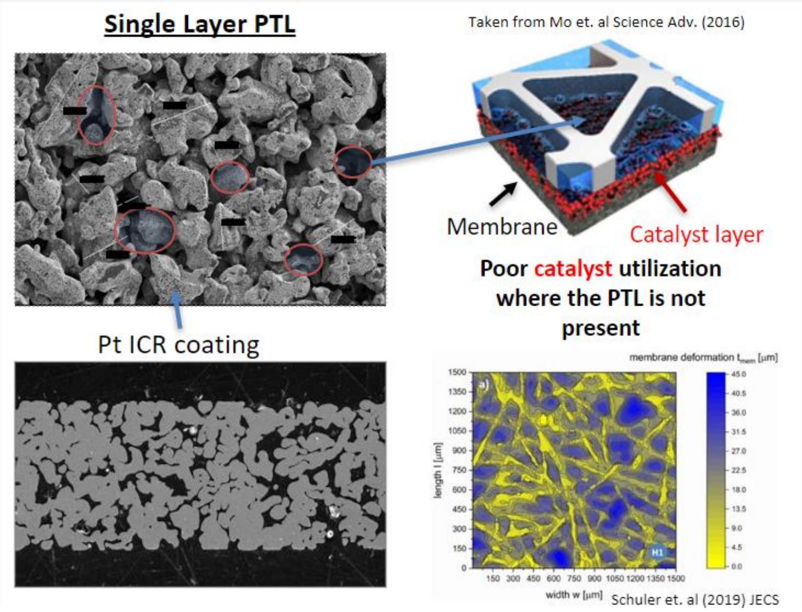
Taken from Trotochaud et al. *J. ACS* (2014)

Current Collectors and Bipolar Plates and how they differ from PEM Systems

Porous Transport Layers serving as current collectors for PEMWE

Figures of Merit

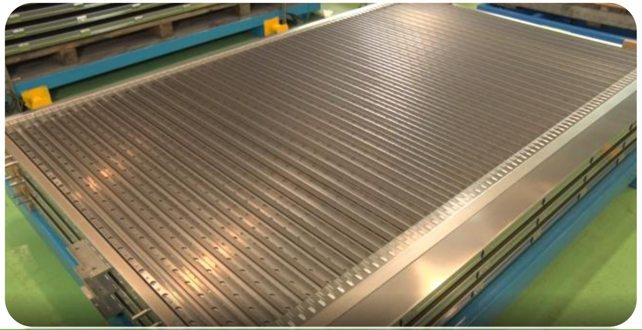
- Ohmic
- Mass Transport
- Mechanical (1500 cm^2)
- Thermal
- Interfacial Roughness
- Porosity



versus Current Collectors (Advanced-AWE)

Figures of Merit

- Structural-Ohmic (welding vs. compression)
  - Avoid hot spots
- Mechanical (3 m^2)
  - Need for elasticity and rigidity (differential pressure)
- Chemical
  - Inhibit oxidation through welding or coatings
- Manufacturability
  - Scale of the components
  - Nickel-plated components



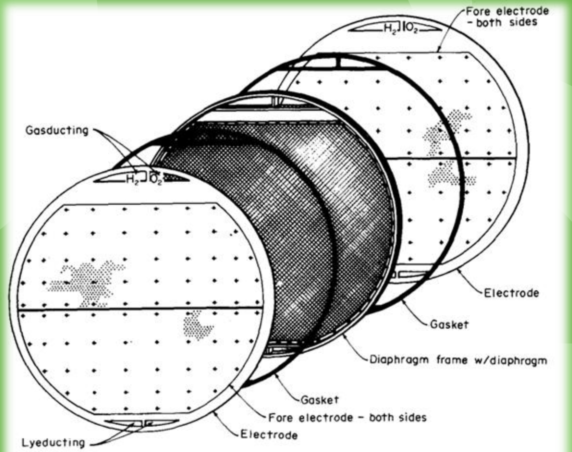
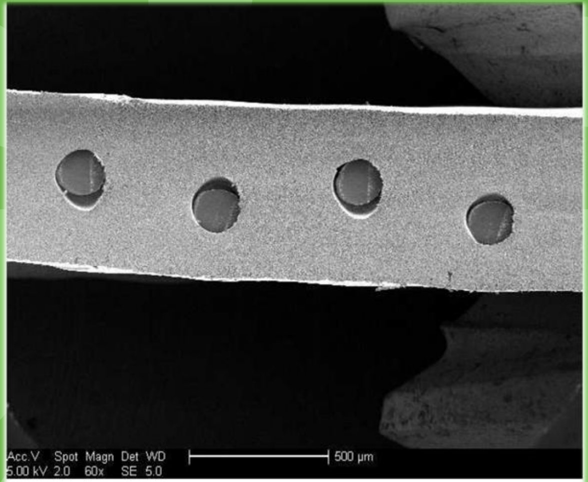
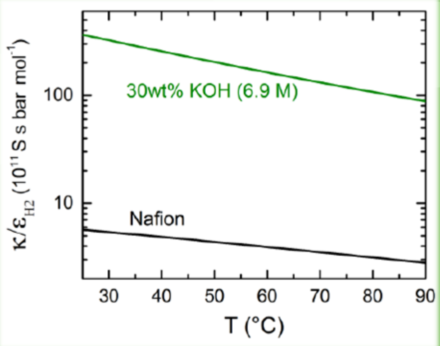


FIG. 1. Norsk Hydro electrolyzer. Exploded view of an electrolyzer cell.



Cross- section of a ZIRFON Perl 500 UTP separator



Separators and Electrolytes in Alkaline Water Electrolysis

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From Asbestos to Zirfon® Note: Carcinogenic asbestos was phased out. This led to a transitory period where PPS fabrics mainly replaced the diaphragms in AWE systems – until reinforced and hydrophilized inorganic oxides were realized

What properties matter for AWE:

- Durability (Mechanical &Chemical)
  - Handling (reinforcement + flexibility)
- Pores (Pore Size, Pore Distribution, Porosity)
- Thickness
- Electrical Resistance

Comparison to PEMWE (Solid Polymer Electrolytes)

- Conductivity is more dependent on liquid KOH
- Gas permeability must be better controlled for
- Thermochemical and thermomechanical degradation mechanisms differ

Top: Grundt et al. *Int. J. Hydrogen Energy* (1981). Middle: de Groot . Bottom: Schalenbach et al. *Int. J. Electrochem. Sci.* (2018)

Open Challenges for Diaphragm|Electrode Interfaces

Areas to improve understanding

- Bubble management (even nanobubbles)
  - In the electrolyte
  - On/around the electrode
- Electrode Geometries
  - Current Distribution
- Concentration gradients?
- Modelling the interface

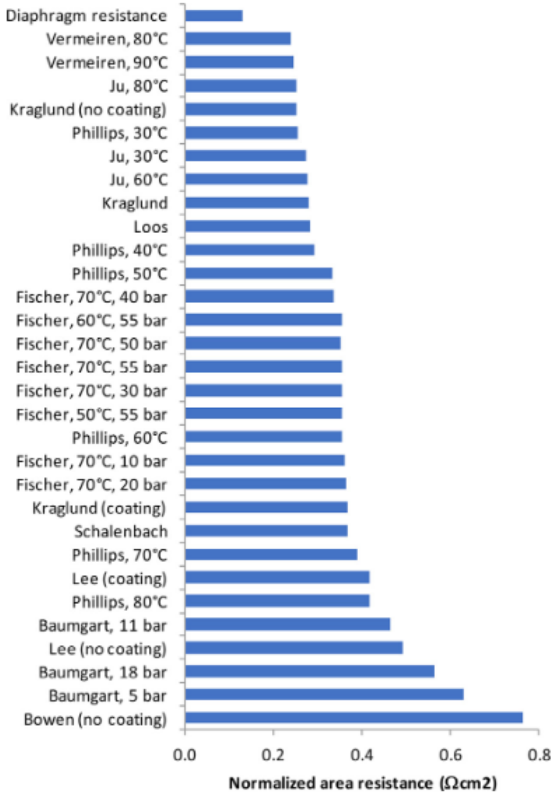

Fig. 4. Comparison of normalized area resistance for different zero gap alkaline electrolyzers (blue bars). All area resistances are normalized to 30 wt% KOH and 80 °C. The depicted diaphragm resistance is 0.13 Ω cm^2 (based on work of Vermeiren). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

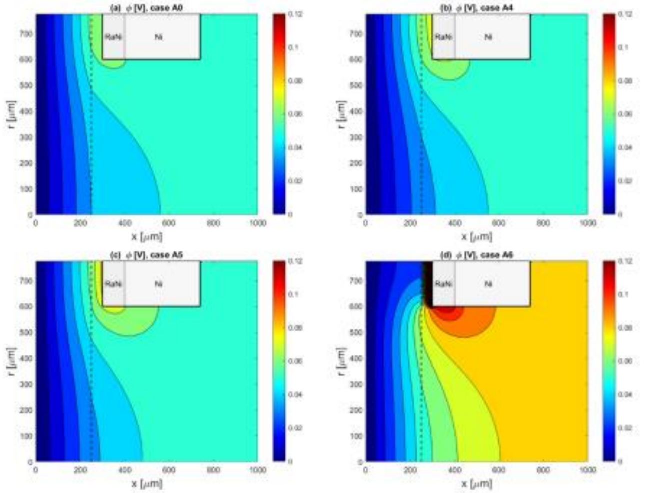

Fig. 5. Contours of the potential ϕ [V]. Results from simulations A0 (a), A4 (b), A5 (c) and A6 (d). The contour increment is 0.01 V. Values above the maximum of the color range (0.12) are also indicated by dark red. The dashed demarcation line at $x = 250\ \mu m$ represents the diaphragm surface. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

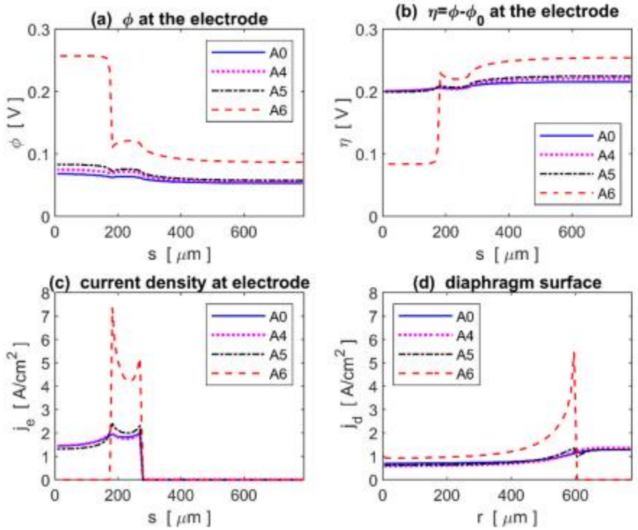

Fig. 6. The profiles of the potential ϕ at the electrode (a), the overpotential η (b), the current density at the electrode (c) and the current density through the diaphragm surface (d), for cases A0, A4, A5 and A6.

Both taken from de Groot et al. *Electrochemica Acta* (2020)

Operating Conditions (variable)

Temperature

Current Density

Load Profile (Intermittency)

Electrolyte (KOH)

Materials Selection (variable)

Nickel

Ni Plated SS

Polymeric Choices

Standardization of Testing Protocols

Sustainability (reduction and recycling of CRMs)

…system-level challenges addressed in another presentation

Integration & Sustainability Challenges

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- **Individual component advancements must be realized by their integration into the stack, for every customer**
- Remaining issues are compounded as the stack becomes longer and larger
  - Hydrodynamics
  - Mechanical Tolerances
  - Sealing
  - Power Control & Distribution
  - Efficiency Losses (shunt/parasitic currents)
- Intermittency plays a role at the system, stack, and component level
  - Displays the need for standardized testing protocols

Recycling Critical Raw Materials

- Benefits
  - Secondary supply, reducing reliance on primary supply and alleviates environmental burdens
- Challenges
  - Different metals require different recycling technologies amidst varying rates

Wrap up

- Lessons learned from adjacent applications can be leveraged as sources of inspiration
- Traditional AWE ≠ Advanced AWE
- There remains improvements to be made on each component, on each interface, and on each scale
- Integration of advanced components into new designs is not trivial
- Sustainability is paramount

Thank you!


We are
DE NORA
EXCITING
SUSTAINABILITY
PARTNER OF CHOICE
CONTINUAL IMPROVEMENT