Introduction to Liquid Alkaline Electrolysis

Marcelo Carmo
NEL Hydrogen

DOE Hydrogen Energy Earthshot Experts Meeting on Advanced Liquid Alkaline Water Electrolysis – January 26-27, 2022

Outline

1. Quick History of Electrolyzers
2. Hydrogen paving the way to Renewables
3. Principles of Alkaline Electrolyzers
4. Two Highlights to catalyze innovation (Diaphragm + Electrodes)
5. Trajectory vs. PEM Technology

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- How far ago?

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www.elsevier.nl/locate/jelechem

Journal of Electroanalytical Chemistry 476 (1999) 90–91

JOURNAL OF ELECTROANALYTICAL CHEMISTRY

Short Communication

Water electrolysis: who first?

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A word can certainly change the interpretation, sometimes even the course, of history. The former seems definitely to be the case with the verb I used [1] referring to Nicholson and Carlisle's experiment: 'discovered' (water electrolysis). I should have more appropriately (and more cautiously) used the word 'observed'.

before Volta, electricity and chemistry ever met. This had occurred sporadically with the application of electrical sparks from Leyden jars to chemical substances. The oldest citation is that mentioning the experiments of Father Beccaria around 1750 (quoted by Priestley in 1772). Father Beccaria observed that an electric discharge could 'revivify' metals; he was thus

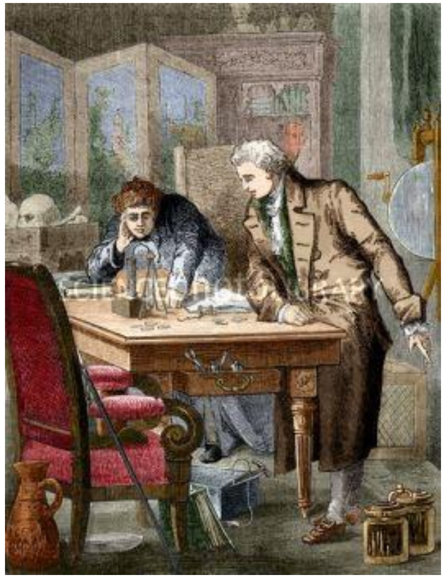
- Who are the main pioneers?

- Volta´s Pile
  - Continuous electrical current
  - Letter to Joseph Banks – 20.03.1800
  - Banks shows to Anthony Carlisle
  - Carlisle was the first to show that Volta was right
  - Carlisle shows to William Nicholson

- William Nicholson and Anthony Carlisle
  - Connected to Nicholson´s doubler
  - Observation of H2 and O2 gas evolution
  - 30 April 1800
  - Filled a small tube with water
  - Inserted Volta´s pile wire
  - Gases formed two inches apart
  - Electrolysis was discovered

The electrolysis experiment demonstrated by Nicholson and Carlisle. Source: Science photo library

Source: Wikipedia



A voltaic pile on display in the Tempio Voltiano Museum, Como, Italy.

Source: Wikipedia

- Alkaline Water Electrolyzers @Scale in the 20th Century

- Long established and well mature technology
- Robust, reliable and safe
- Significantly efficient
- The most extended technology at a commercial level
  - By 1902, more the 400 industrial alkaline electrolysers
  - Primarily for ammonia production (fertilizer industry)
  - Plants based on low-cost hydroelectricity

Aswan Dam – Egypt

Source: Wikipedia

Aswan Electrolyser (KIMA)
165MW - 37000 m³H_2/h

Source: ELT

- Alkaline Water Electrolyzers @Scale in the 20th Century

- 20th century – Ammonia from hydropower
  - Electrolyser plants in Canada, Chile, Egypt, Iceland, India, Norway, Peru and Zimbabwe

- Today only 3 are believed to be in operation
  - Cuzco, Peru
  - Aswan, Egypt
  - Que Que, Zimbabwe
    - → 28 electrolysers
    - → 165 MW
    - → Type S-556
    - → 37000 Nm^3H_2/h
    - → In use over 35 years

- Other industries are still on the market
- Companies acquired or merged with others
- Transferred technologies
- Information is very scarce and contradictory

Zimbabwe Electrolyser
165MW - 37000 m^3H_2/h

Source: KIMA

A Quick History of Water Electrolyzers

- NEL Hydrogen paving the way to green Hydrogen!

1789	- Discovery of water splitting by A. Paets van Troostwijk und J.R. Deimann
1820	- M. Faraday defined the term electrolysis for "water splitting"
1900	- First industrial electrolyzer by O. Schmidt
1920 – 1930	- First electrolysis boom due to high ammonia demand (fertilizers)
1924	- J.E. Noeggenrath was to first to patent high pressure electrolyzer (100 bar)
1925	- M. Raney investigated the activity of catalysts to increase catalyst surface area.
1929	- Norsk-Hydro's (NEL Hydrogen) started hydrogen via electrolysis with earliest bipolar technology
1948	- E.A. Zdansky demonstrated first high pressure industrial electrolyzer (Lonza)
1954-1957	- Winsel and Justi patented Raney-Nickel for Alkaline Electrolyzers
1956-1960	- Largest atmospheric pressure electrolyzer (40.000 Nm^3/h H_2 (200 MW)) in Assuan – Egipt
1972-1974	- Largest high pressure electrolyzer (Lurgi) (21.000 Nm^3/h H_2) in Zimbabwe (100 MW)

- NEL Hydrogen paving the way to green Hydrogen!

Såheim I&II, Rjukan: from 1929

Up to 16500 Nm^3/h and 88 MW_{el}

- NEL Hydrogen paving the way to green Hydrogen!

Rjukan, Norway (1927 – 1970s)

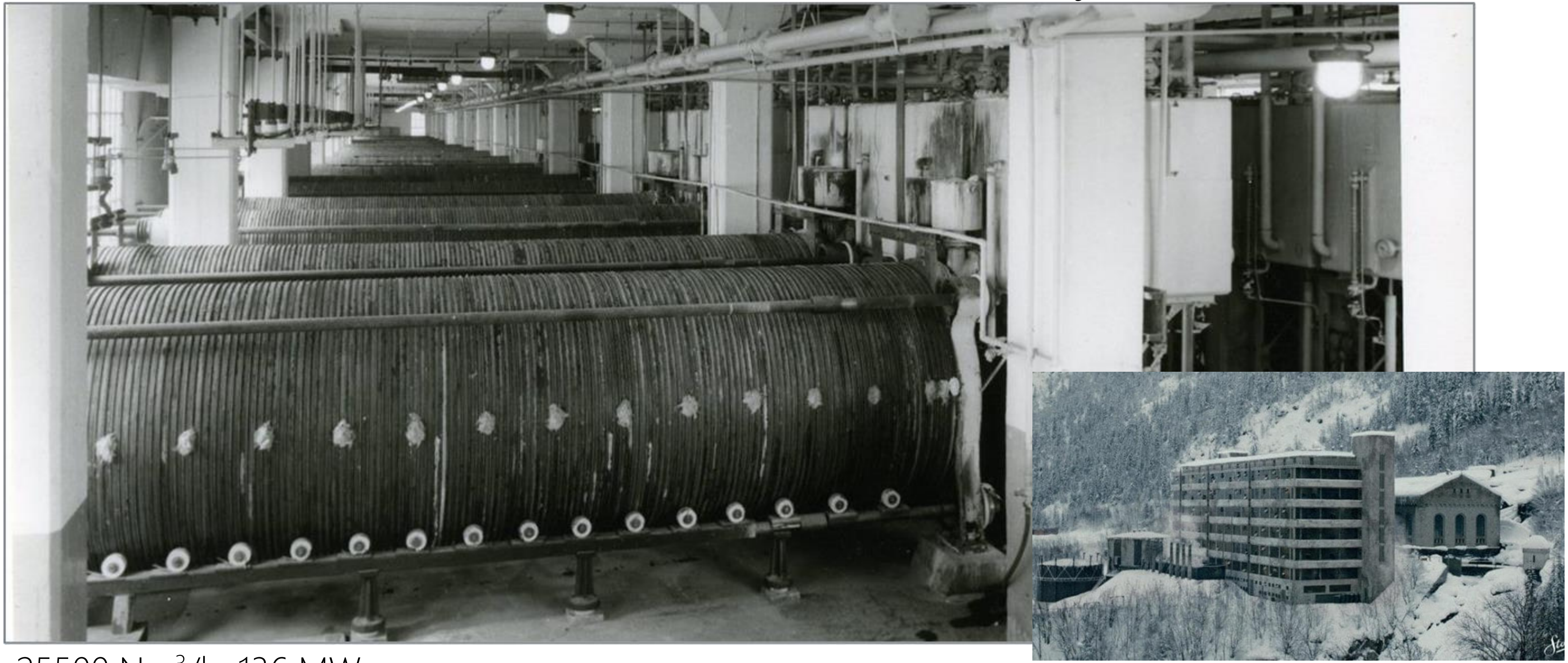
Glomfjord, Norway (1953 – 1991)

- Two largest electrolyser plants worldwide
- Capacity: 30.000 Nm3/h each
- Energy consuption: 135 MW each
- Electrolycity source: Hydropower

A Quick History of Water Electrolyzers

- NEL Hydrogen paving the way to green Hydrogen!

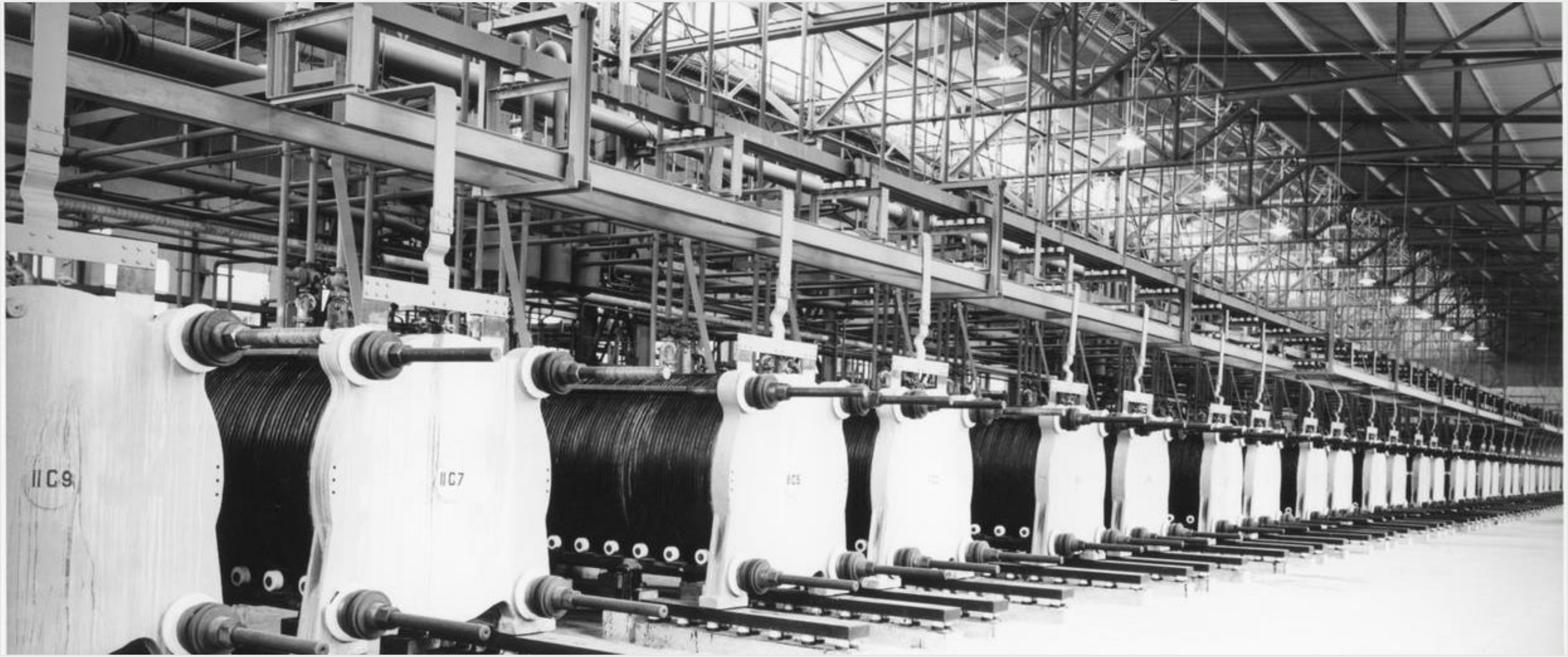
Vemork, Rjukan: from 1928 to 1971



25500 Nm^3/h, 136 MW_{el}

- NEL Hydrogen paving the way to green Hydrogen!

Glomfjord: from 1948 – 1993



27100 Nm^3/h and 142 MW_{el}

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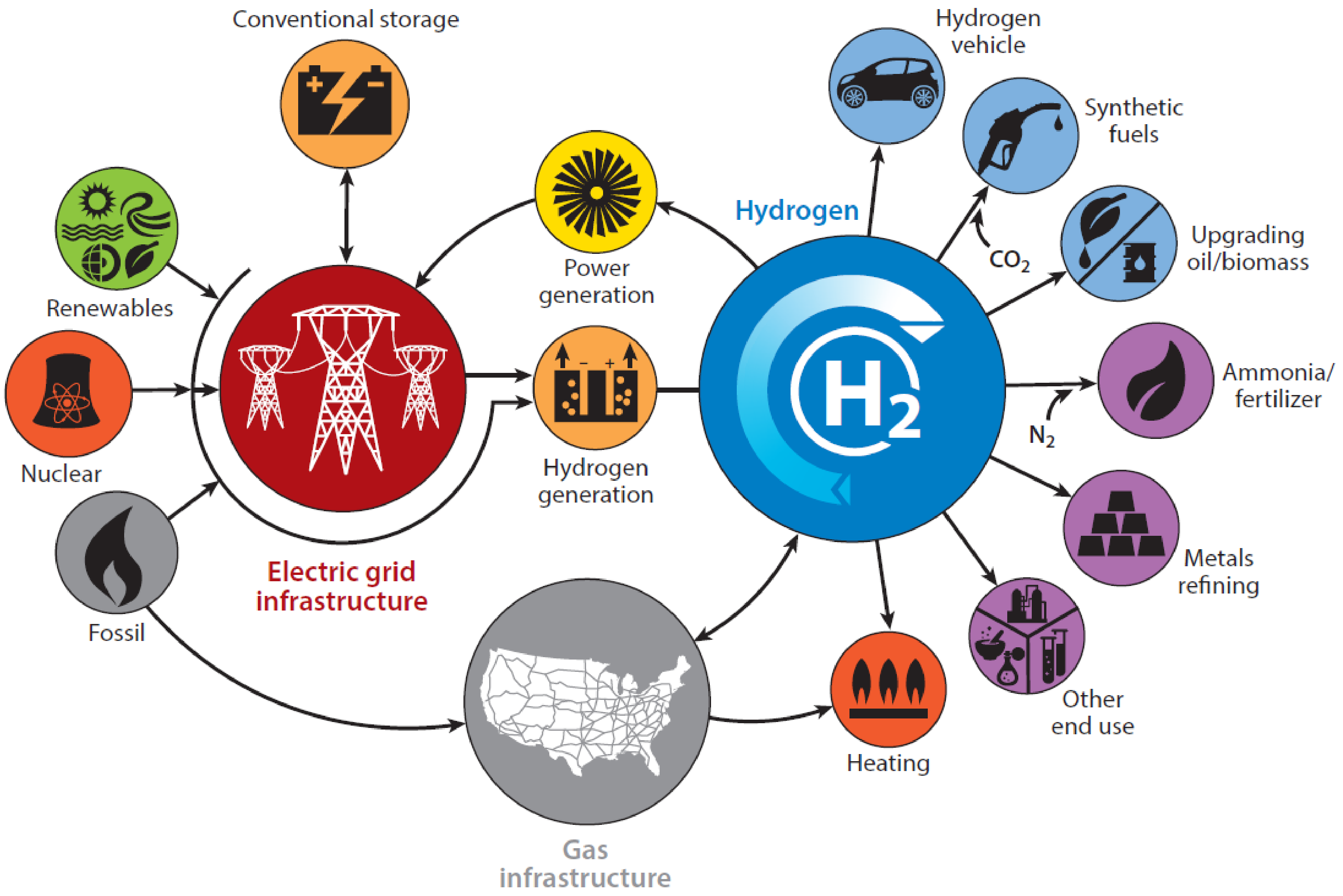
Hydrogen paving the way to Renewables

- US Department of Energy's H2@Scale initiative

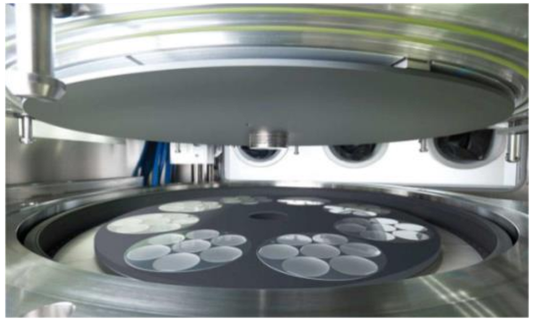


Source: B. Pivovar, DOE H2@Scale, www.energy.gov

Markets grow as unit scale increases

Analytical Labs

Weather Balloon Filling



Industrial Processes

Heavy Duty Vehicle Fueling

Power Plant Cooling

NEL Hydrogen – A key player in the generation of green hydrogen

- Iberdrola, Spain; Renewables → Green Hydrogen (20 MW PEM) → Ammonia

Nel and Aibel team for Iberdrola plant to kick off green hydrogen pact

Electrolyser maker and oil & gas services company to jointly develop and deliver large green hydrogen projects

28 April 2021 10:39 GMT *UPDATED 28 April 2021 11:32 GMT*

By Bernd Radowitz

Electrolyser maker Nel and oil & gas services company Aibel signed a framework agreement to work together on large-scale renewable hydrogen projects.

To kick off their alliance the two Norwegian groups will work jointly to deliver a 20MW PEM hydrogen production plant to Iberdrola to provide green hydrogen for industrial use in a link-up with fertiliser group Fertiberia that was first announced last summer by the Spanish utility.

"We are very excited to be announcing this collaboration with Aibel, a company with vast experience in delivering large scale, complex projects across industries," Nel chief executive Jon André Løkke said.

Renewables giant Iberdrola to build 'Europe's largest green hydrogen project'

Read more

"Their in-house construction expertise and experience in fabrication and modularisation will add significant value to Nel's global delivery and project execution abilities."

Løkke added the partnership is a long-term commitment. Beyond the work for Iberdrola, Nel is phasing in Aibel on selected ongoing projects.

The agreement represents a strategic step in Aibel's transformation towards renewable energy segments, the service provider's CEO Mads Andersen said.

PEM Electrolyser Containerized Solution

NEL Hydrogen – A key player in the generation of green hydrogen

- Sunline Transit, Renewables → Green Hydrogen (2 MW PEM) → Bus Refueling

Nel ASA: Awarded USD 8.3 million Hydrogen Electrolyser Fueling Station Contract

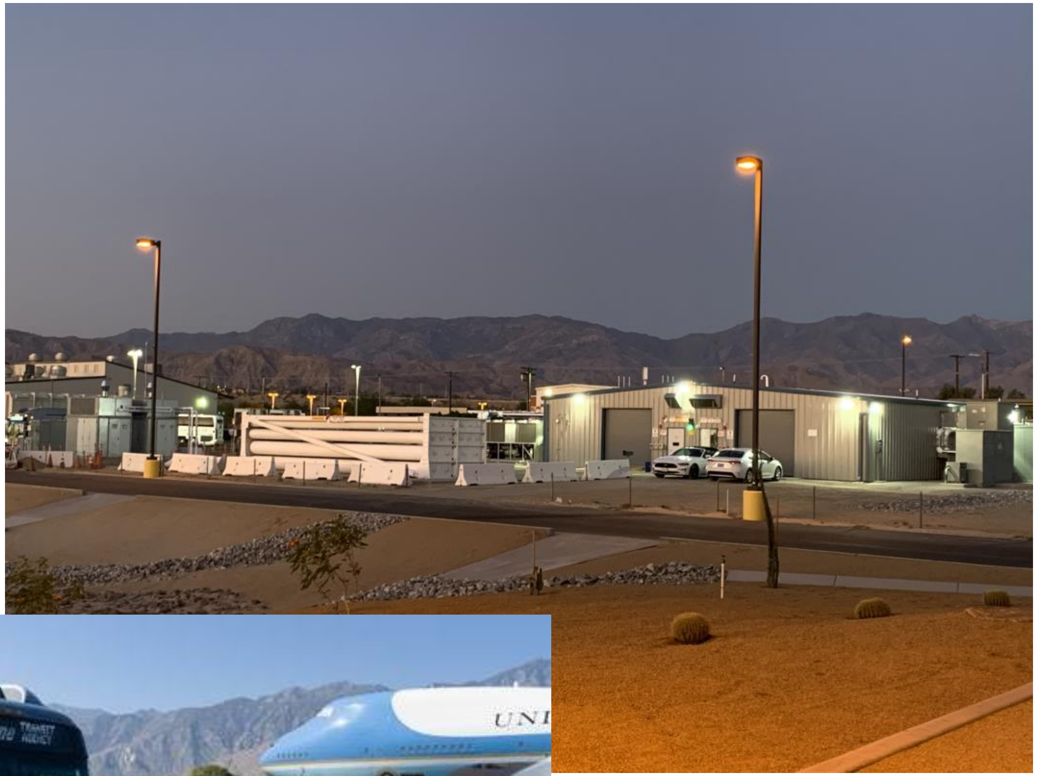
(Oslo, 25 September 2017) Proton Onsite (Proton) and Nel Hydrogen Solutions, divisions of Nel ASA (Nel, OSE:NEL), have received a purchase order of USD 8.3 million on a combined hydrogen PEM electrolyser and H2Station® fueling solution for SunLine Transit Agency (SunLine) in California. The combined solution will have a hydrogen capacity of up to 900 kg per day, making it the world's largest combined hydrogen production and fueling facility currently being contracted. SunLine will use the solution for fueling of their growing fleet of Fuel Cell Electric Buses operating in the Palm Springs area in California.

"We are very pleased to have been awarded this contract to deliver a turnkey hydrogen production and fueling solution to SunLine that will provide zero-emission public transportation for the Palm Springs area and contribute to California's climate efforts. This delivery highlights the combined strengths of Proton and Nel, using cutting-edge technology both within PEM electrolysis and heavy duty fueling solutions for buses," says Jon André Løkke, Chief Executive Officer of Nel.

The facility will be delivered turn-key, consisting of one Proton PEM M400 electrolyser, and two H2Station® units from Nel. The awarded contract has a total value of just over USD 8.3 million, with expected delivery and installation during 2018.

"The project is strategically important for Nel and Proton, as it shows our joint capability in delivering unparalleled hydrogen production and fueling solutions. The combined organization is well-positioned to be part of current and future initiatives needed to achieve California's long-term renewable energy goals," says Løkke.

The project is supported by the Californian Air Resources Board (CARB) under the California Climate Investments (CCI) program.



NEL Hydrogen – A key player in the generation of green hydrogen

- Polysilicon (Malaysia), Renewables→ Hydrogen (25 MW ALK)→ Semiconductors

Using 100% green electricity from Hydroelectricity

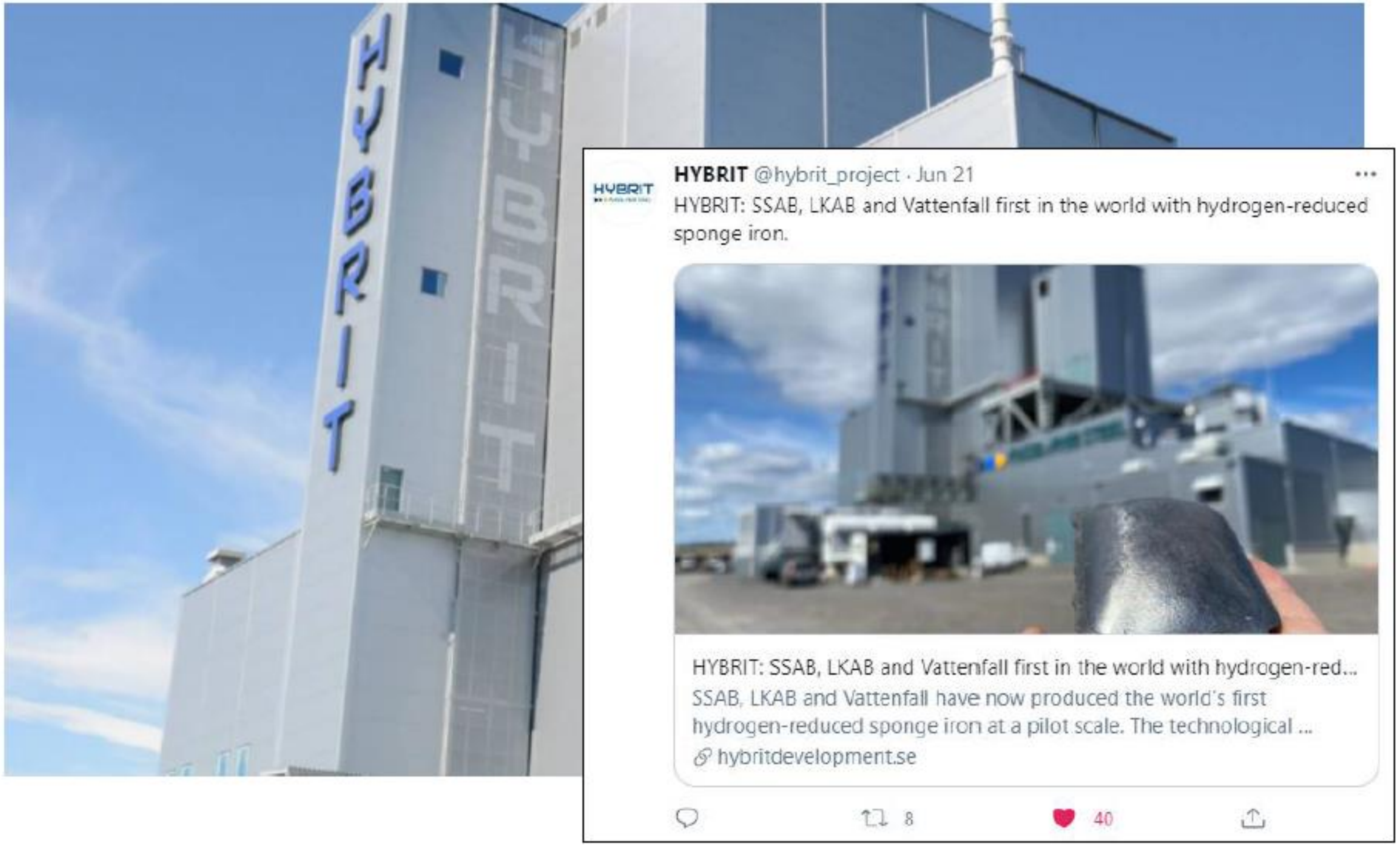
Hydrogen supply is critical for the plant → reliability is paramount

24/7 operation

Biggest water electrolyser in operation globally

Offsetting ~43,000 Tons CO_2/y

- HYBRIT - Sweden, Renewables → Green Hydrogen → Fossil-free steel project



Supplying electrolysers to the currently most advanced fossil-free steel project

- Nel has received a purchase order for a 4.5 MW alkaline electrolyser which will be used in a pilot plant for fossil free steel production
- Hybrit Development AB (HYBRIT) is a joint venture owned equally by SSAB, LKAB and Vattenfall
- The steel industry accounts for 7% of global and 10% of Swedish CO2-emissions
- Pilot plant will operate in Luleå, Sweden from 2021 – 2024, with target of full-scale implementation by 2035

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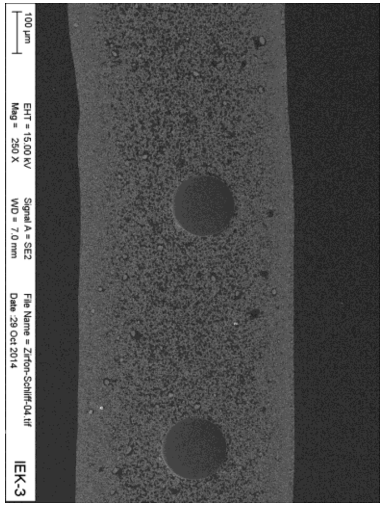
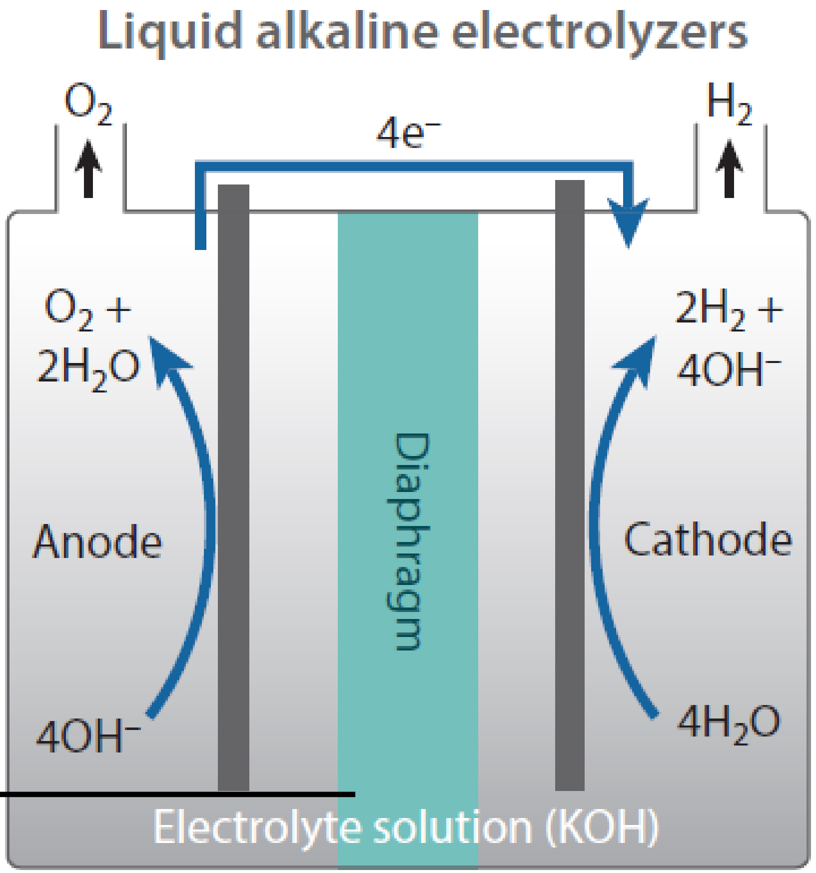
Principles of Alkaline Water Electrolyzers

- Alkaline *vs.* PEM



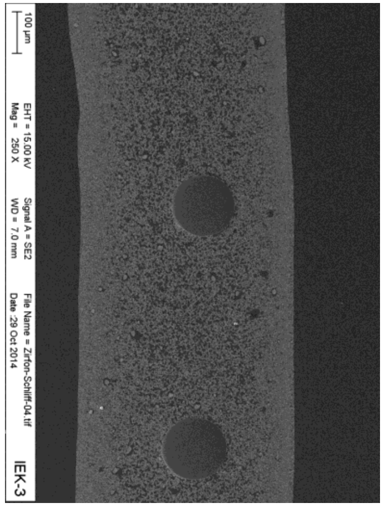


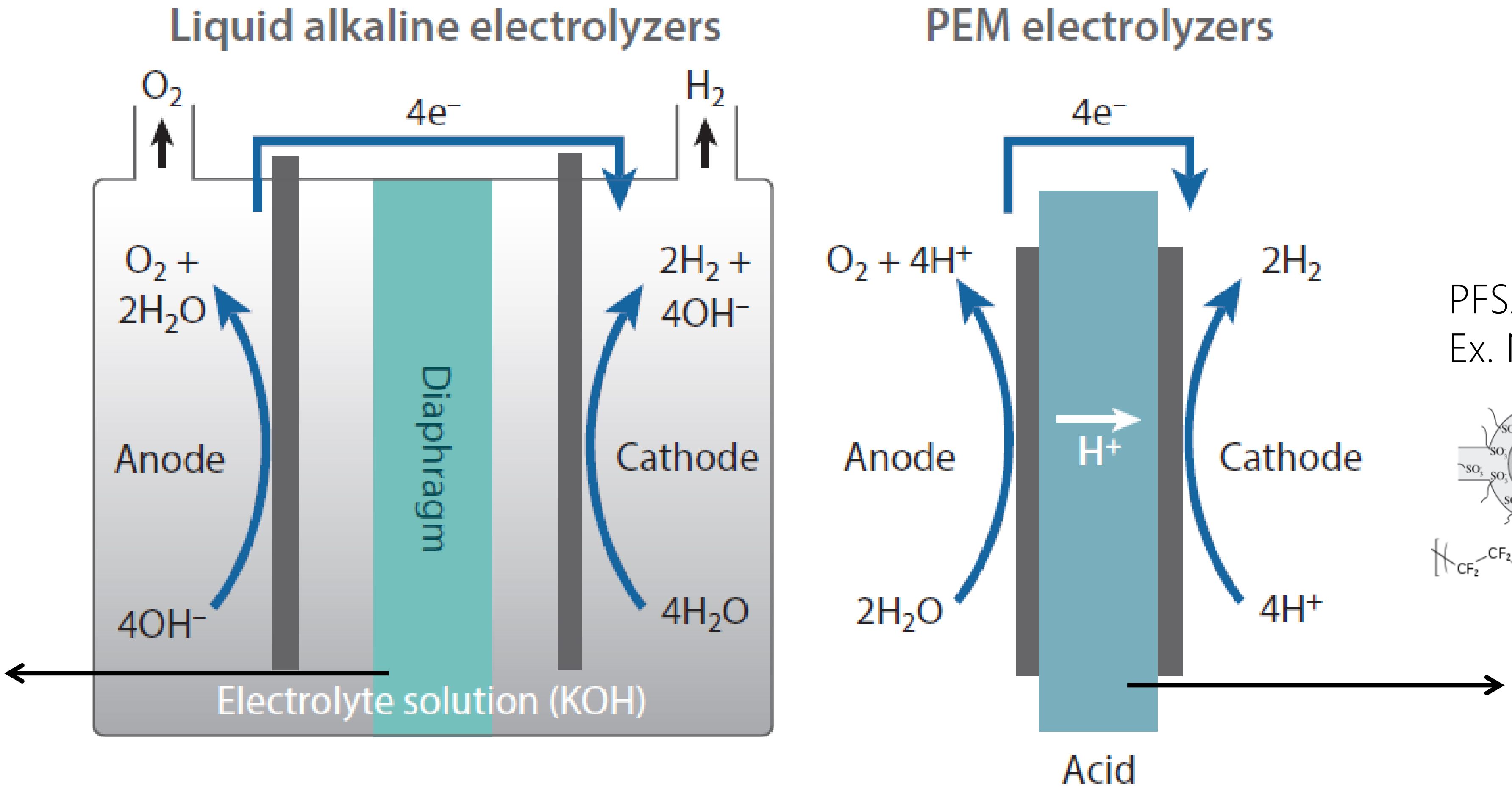
Anode $4OH^- \longleftrightarrow 2H_2O + O_2 + 4e^-$

Cathode $4H_2O + 4e^- \longleftrightarrow 2H_2 + 4OH^-$

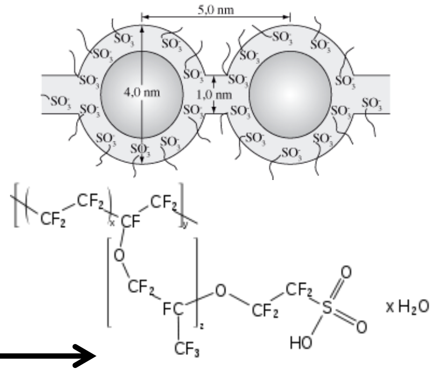
Principles of Alkaline Water Electrolyzers

- Alkaline *vs.* PEM





PFSA membranes:
Ex. Nafion



Anode $4OH^- \longleftrightarrow 2H_2O + O_2 + 4e^-$

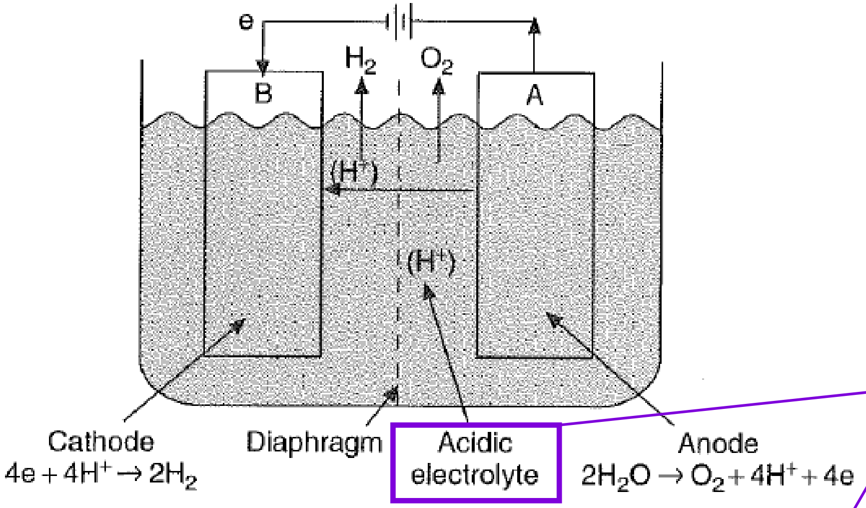
Cathode $4H_2O + 4e^- \longleftrightarrow 2H_2 + 4OH^-$

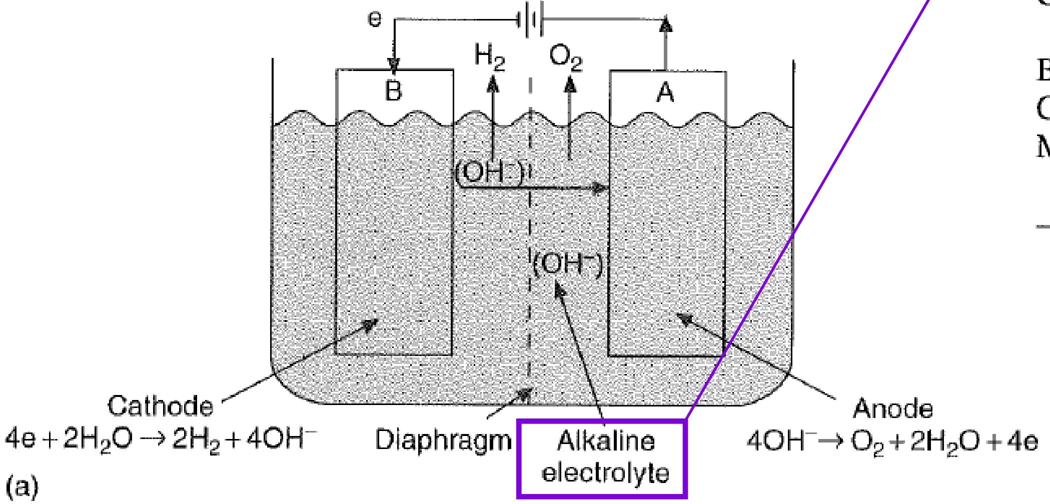
Anode $2H_2O \longleftrightarrow O_2 + 4H^+ + 4e^-$

Cathode $4H^+ + 4e^- \longleftrightarrow 2H_2$

Principles of Alkaline Water Electrolyzers

- OH^- vs. H^+ Electrolytes



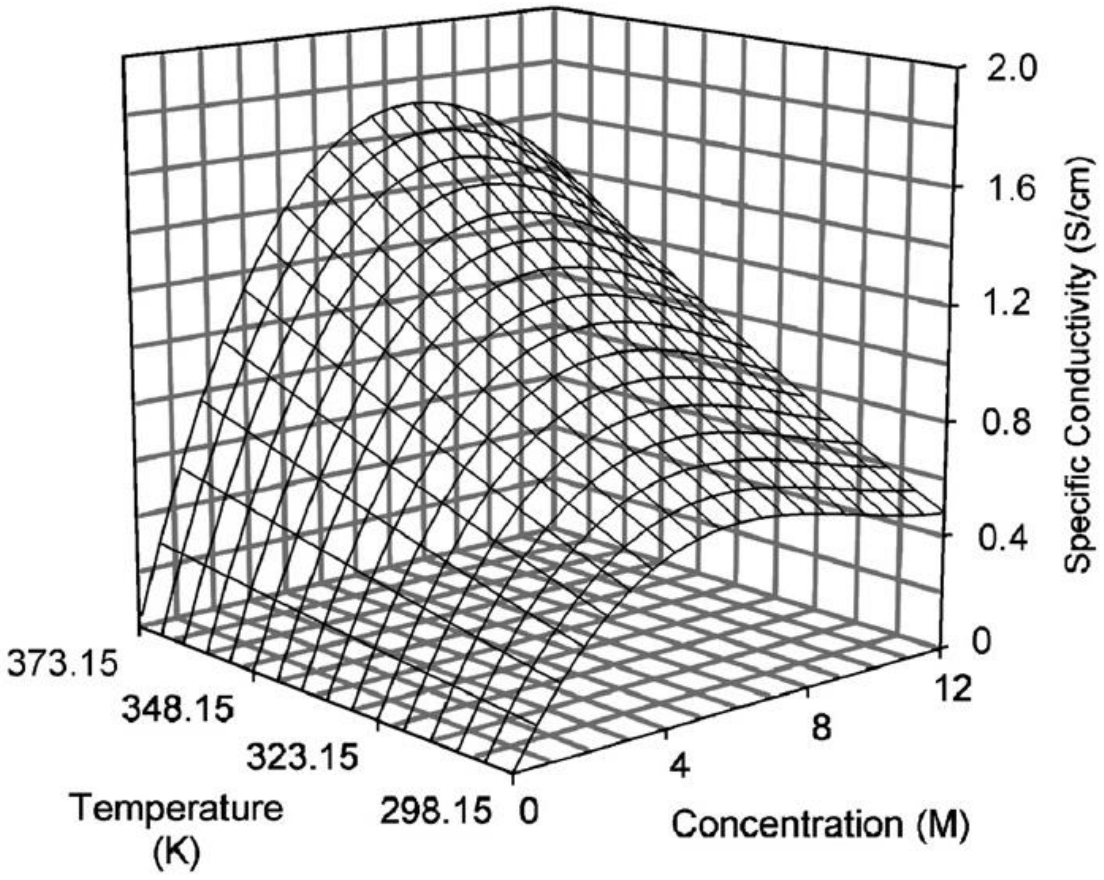


(a)

Table 1.

Ion	λ_0^+, λ_0^- / Ω^{-1} mol^{-1} cm^2	Ion	λ_0^+, λ_0^- / Ω^{-1} mol^{-1} cm^2
		Ag^+	62.2
H^+	349.8	Na^+	50.11
OH^-	197	Li^+	38.68
K^+	73.5	$[Fe(CN)_6]^{4-}$	440
NH_4^+	73.7	$[Fe(CN)_6]^{3-}$	303
Rb^+	77.5	$[CrO_4]^{2-}$	166
Cs^+	77	$[SO_4]^{2-}$	161.6
		I^-	76.5
Ba^{2+}	126.4	Cl^-	76.4
Ca^{2+}	119.6	NO_3^-	71.5
Mg^{2+}	106	CH_3COO^-	40.9
		$C_6H_5COO^-$	32.4

- Electrolyte Concentration and Temperature of Operation



Points to consider:

- Responsible for great Ohmic losses
- Ionic transfer depends on electrolyte conc.
- Distance between the different layers
- Presense ob bubbles (sizes)
- Viscosity/Surface tension (additives)
- Interaction with the diaphragm
- Temperature distribution
- Recirculation
- Leakage
- Advantages when monopolar conf. is used
- Evaporation
- Corrosion
- Safety issues

- Different types of diaphragms

Requirements for using diaphragms:
- High gas separation efficiency
- High chemical stability
- High mechanical and thermic stability

Property / Material	Type	Temperature [°C]	Thickness [µm]	Specific Resistance [Ωcm²]	Remarks
Plain Asbestos	inorganic	<100	2000 - 5000	0,74	hazardous
Polymer-reinforced Asbestos	composite	<100	200 - 500	0,15 - 0,2	superior chemical resistance and mechanical stability in comparison to plain asbestos
PTFE-bonded potassium titanate	composite	120 - 150	300	0,1 - 0,15	shows excellent stability in hot caustic environment
Polymer-bonded zirconia	composite	<160	200 - 500	0,25	ZrO_2 on polyphenylsulfon lattice

- Electrode Developments

- Circular bipolar plate (~1.8 m in diameter) with gas-ducts at top and lye ducts at bottom
- Electrodes on both sides fixed to bipolar plates with through connection bolts
- Rubber frames with inlet/outlet channels
- Electrodes and bipolar plate of mild steel coated with nickel
  - Nickel-plating key in production technology
- Anodes: activated nickel
- Cathodes: SU-coating
  - Developed by Norsk Hydro in 1950-1960's and increased production output by 30%
- Electrode activation and nickel-plating is core technology and carried out at Notodden, Norway

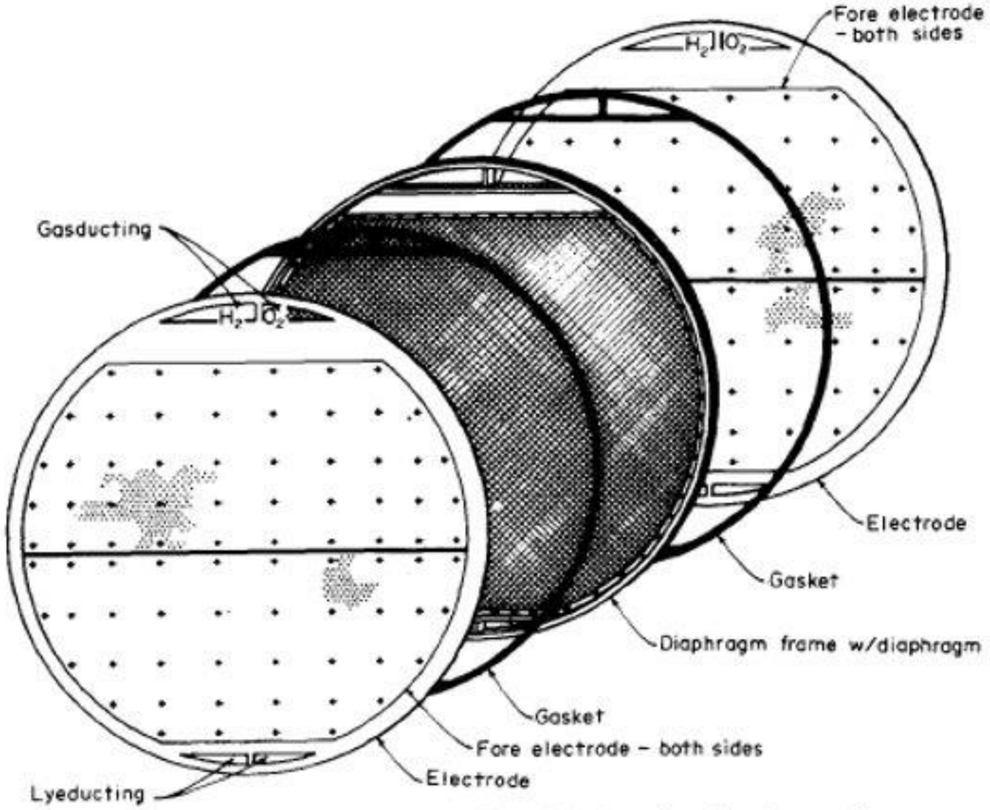


FIG. 1. Norsk Hydro electrolyzer. Exploded view of an electrolyzer cell.

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World largest AEL plant in operation

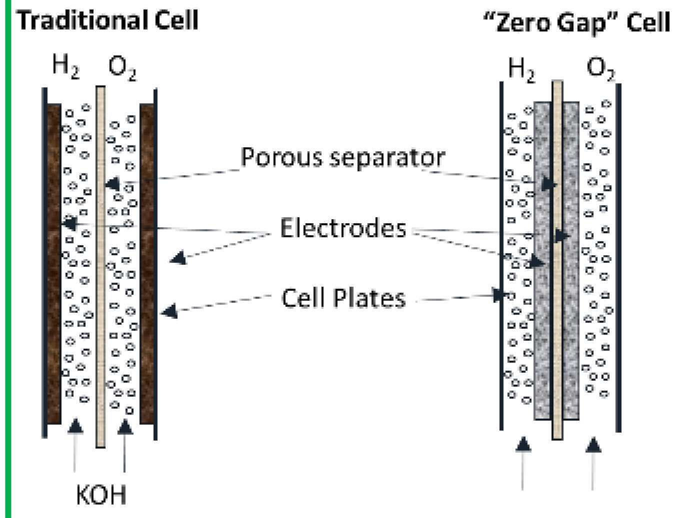
- Tokyama plant 25 MW – 12 t/d

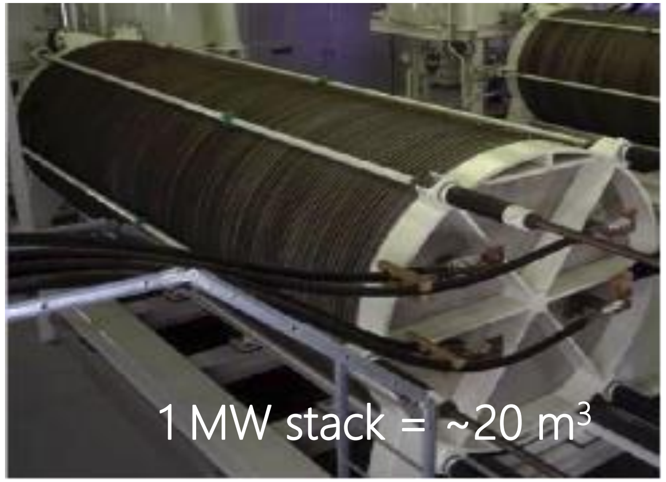
Largest AEL plant in operation in Europe 2020

- Akzo Nobel/Nouryon, Norway - Chemicals – 1.940Nm3/h - 9.2MW

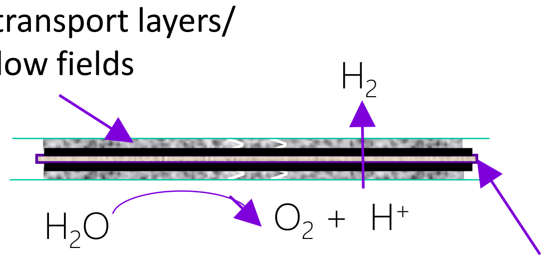
- Commercial technologies

- Liquid KOH (base):
  - Catalysts are common metals
  - Corrosive electrolyte
  - Low output, high efficiency





- Proton exchange membrane (PEM/acid):
  - Catalysts are rare metals
  - High output, benign electrolyte

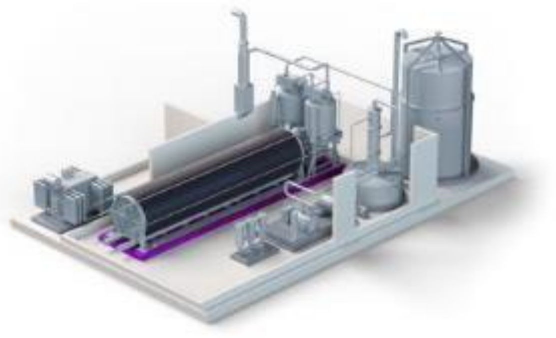


1 MW stack < ~0.5 m^3

Commercial low temperature (50-80C) – MW scale, demonstrated reliability

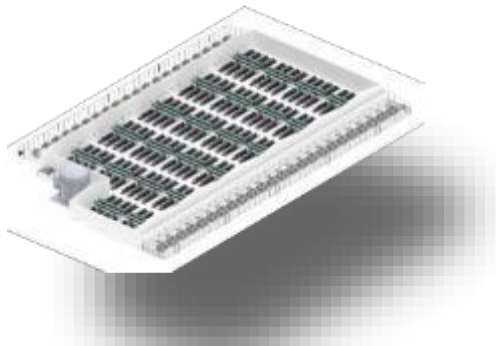
NEL HYDROGEN ELECTROLYSER

- Alkaline product scale



1 electrolyzer (2.2MW)

Built for future expansion up to any capacity size



176 electrolyzers (~400MW)

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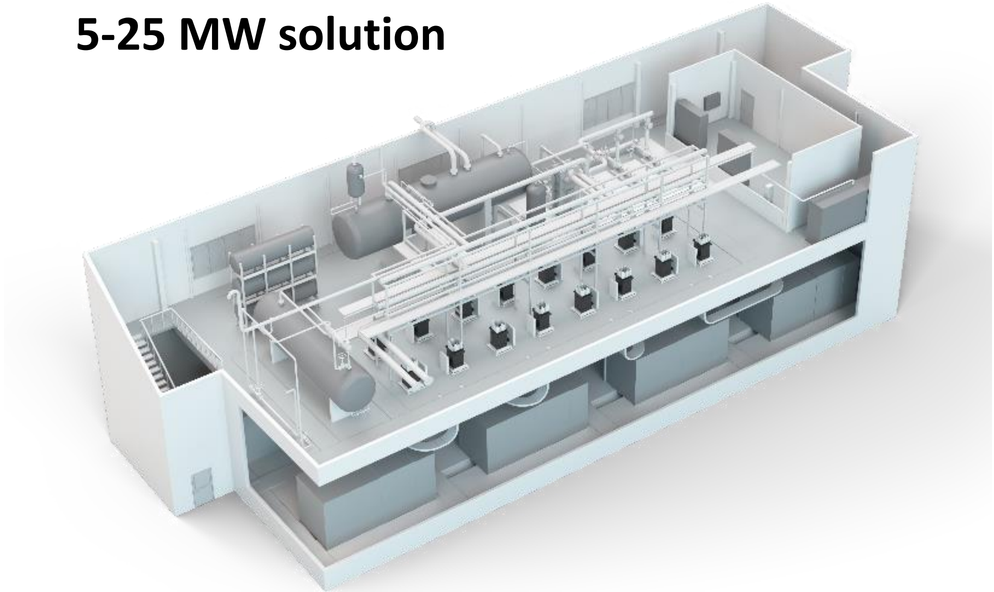
- PEM product scale

M Series

1.25-2.5 MW solution

Larger Installations

5-25 MW solution



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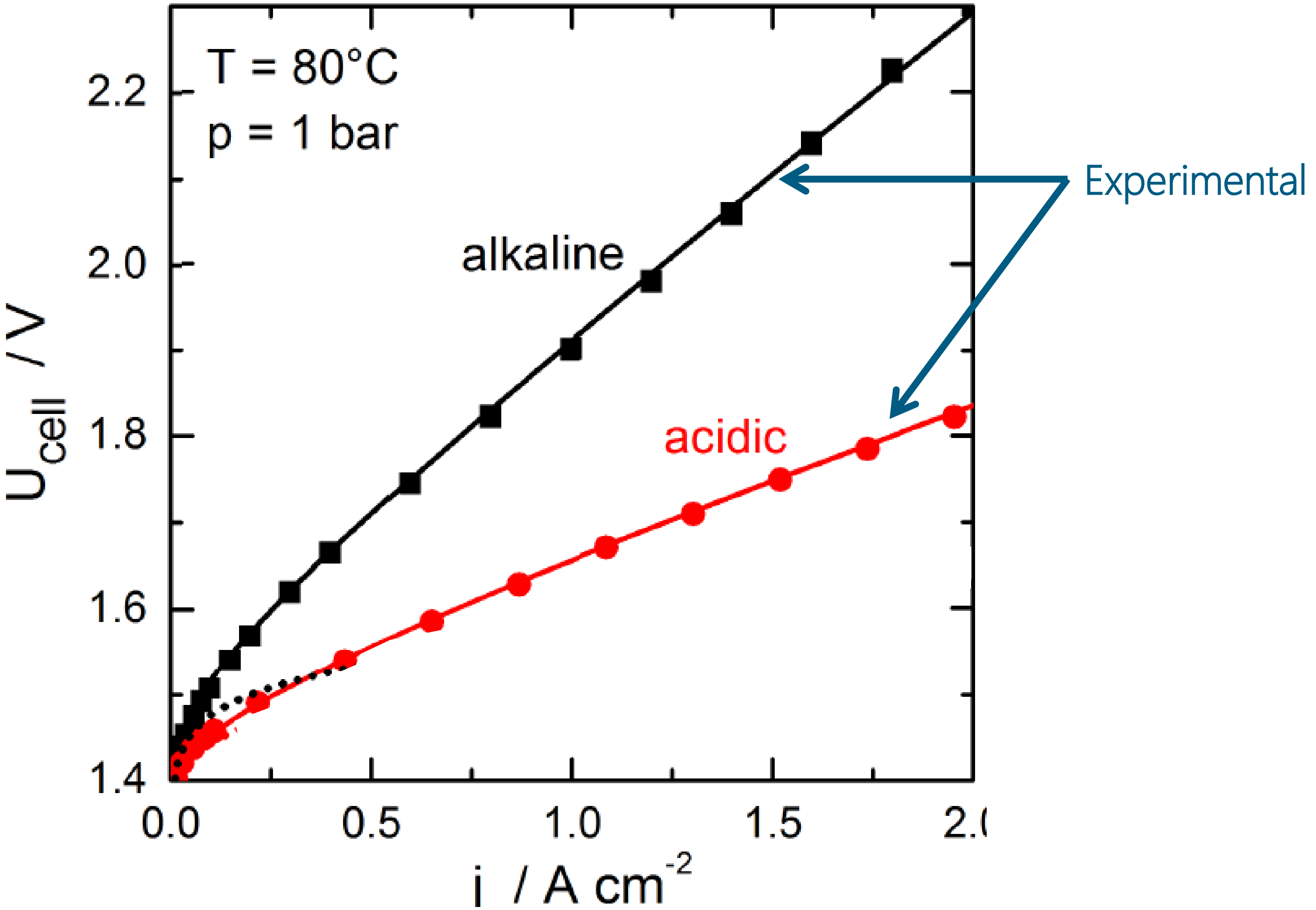
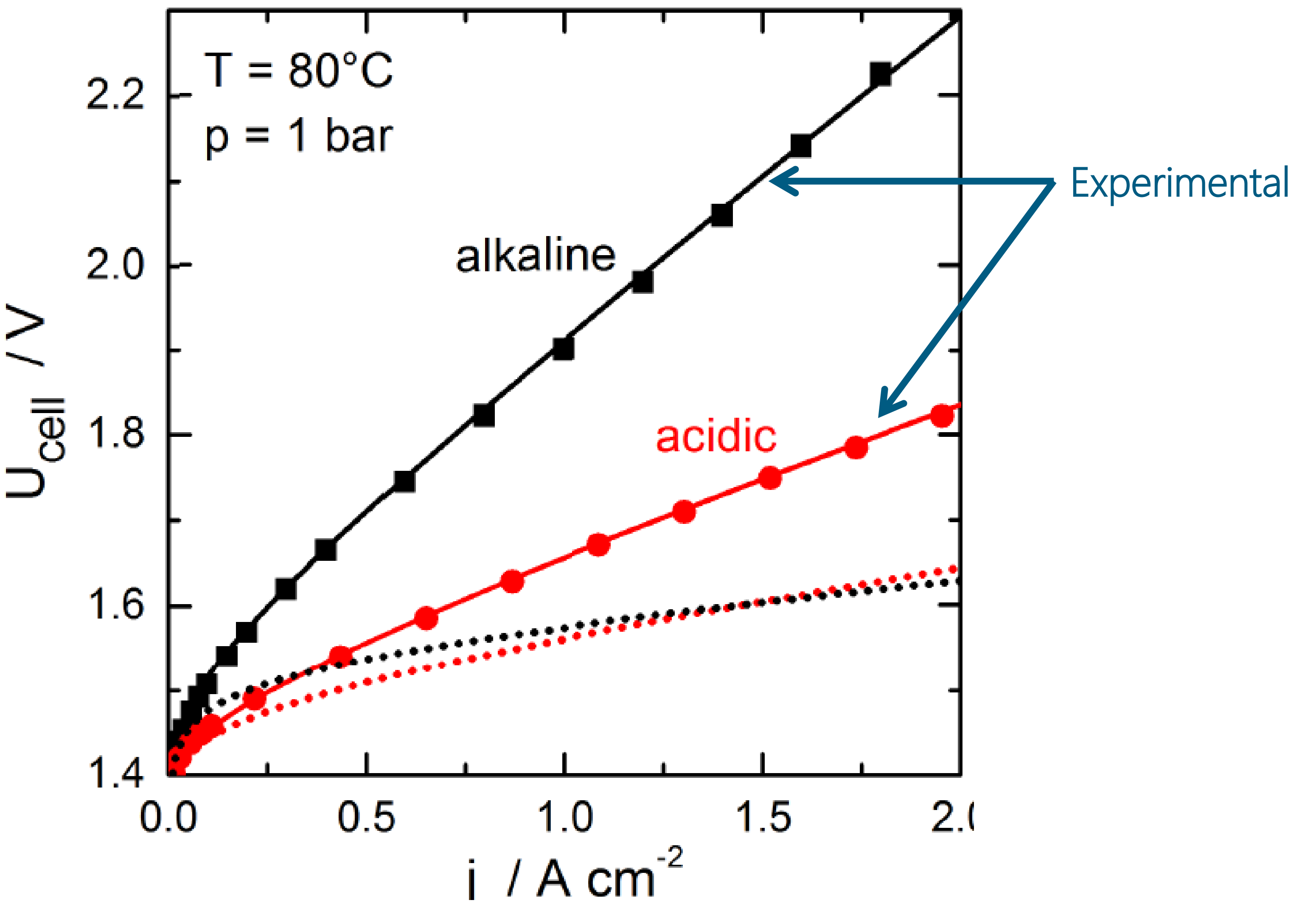
- Alkaline *vs.* PEM – Thickness of the separator/membrane



M. Schalenbach, J. Electrochem. Soc. 2016
volume 163, issue 11, F3197-F3208

- Alkaline *vs.* PEM – Thickness of the separator/membrane



M. Schalenbach, J. Electrochem. Soc. 2016
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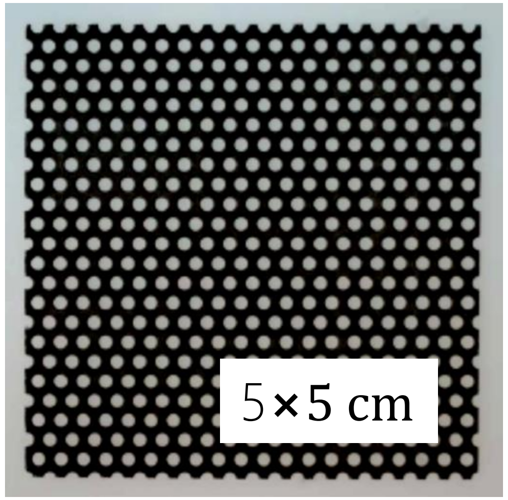
PBI based membranes coupled to Raney-Ni catalysts

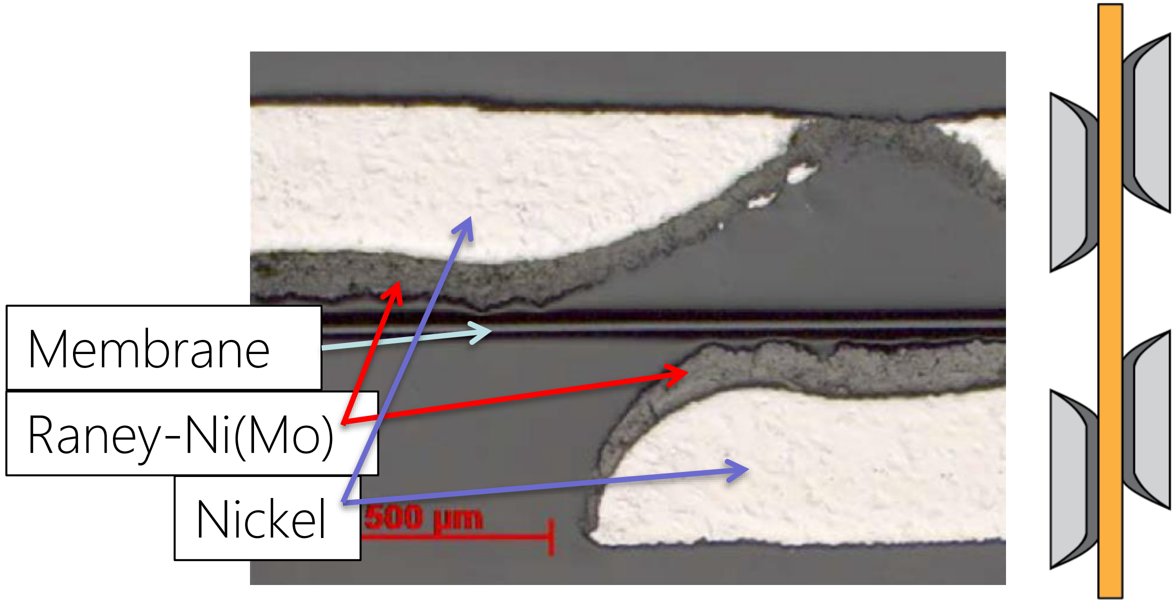
M. Kraglund et al, Energy and Env. Science, 12, 3313, 2019.

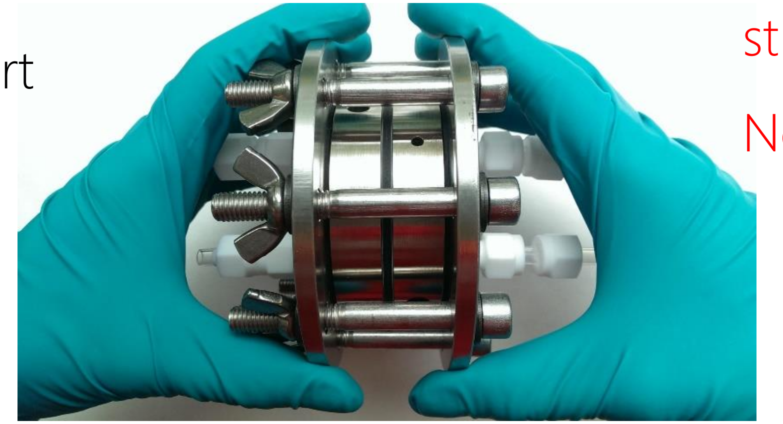
- Ion-solvating membranes

Raney-electrodes by perforated plates



Prepared by DLR Stuttgart by VPS method





Cells operated with strong supporting KOH

No ionomer needed

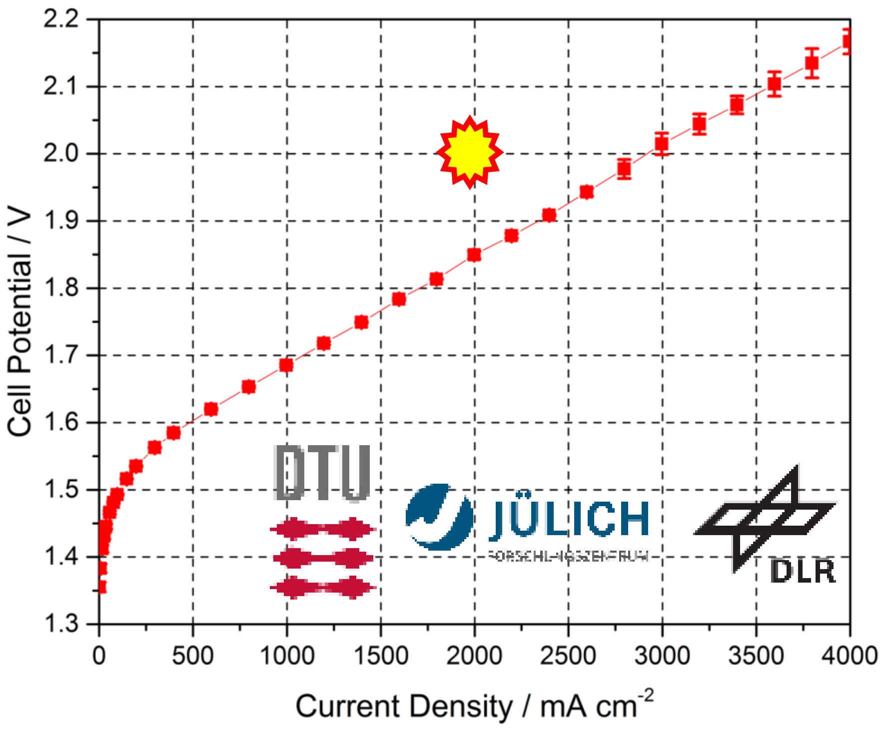
Raney nickel compositions
Cat.: Ni, Al, Mo
An.: Ni, Al

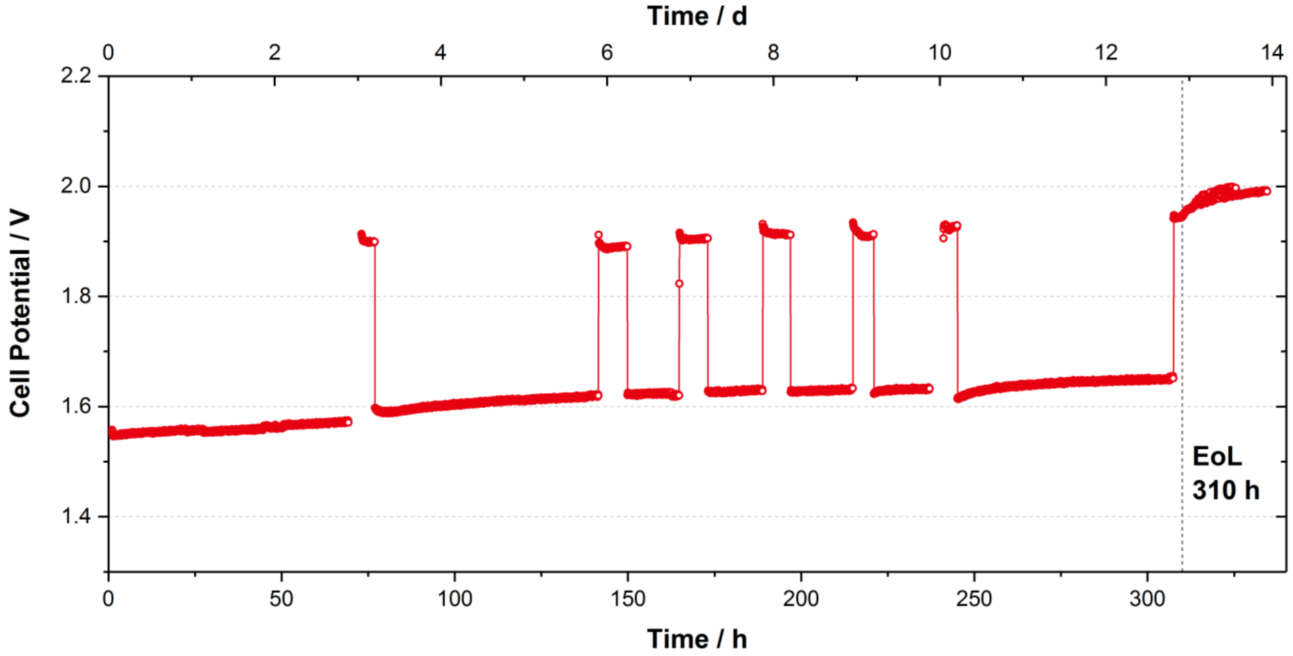
JÜLICH Forschungszentrum
DLR
DTU Energy Technical University of Denmark

PBI based membranes coupled to Raney-Ni catalysts

- Ion-solvating membranes

M. Kraglund et al, Energy and Env. Science, 12, 3313, 2019.





- 24 wt% KOH at 80°C for three different cells. Error bars represent variation across 2 or 3 cells.
- Cells are (cathode/separator/anode): Raney-NiMo/40 µm m-PBI membrane/Raney-Ni anode.

JÜLICH Forschungszentrum DLR DTU Energy Technical University of Denmark DTU

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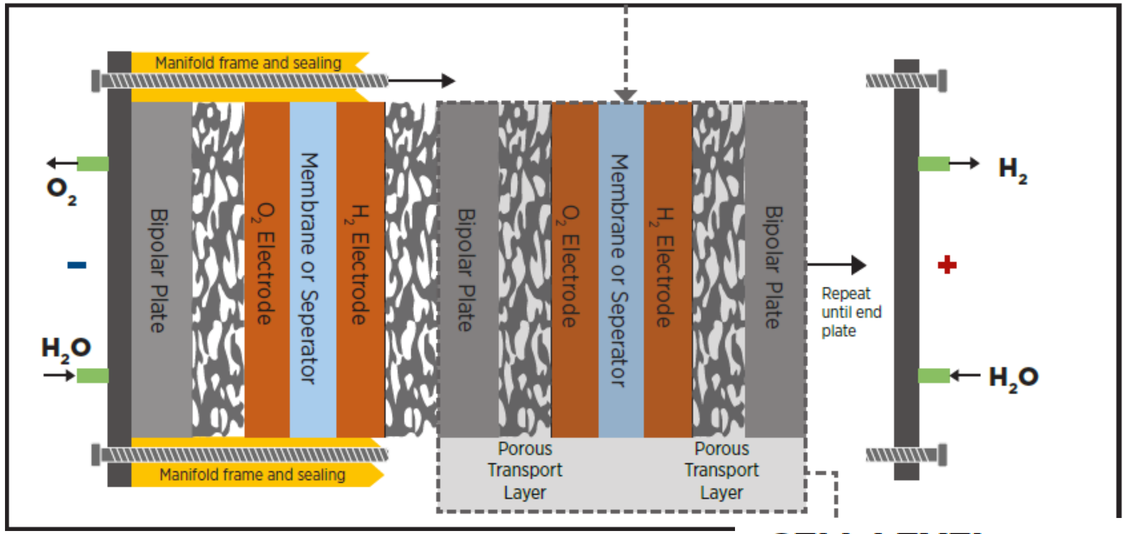
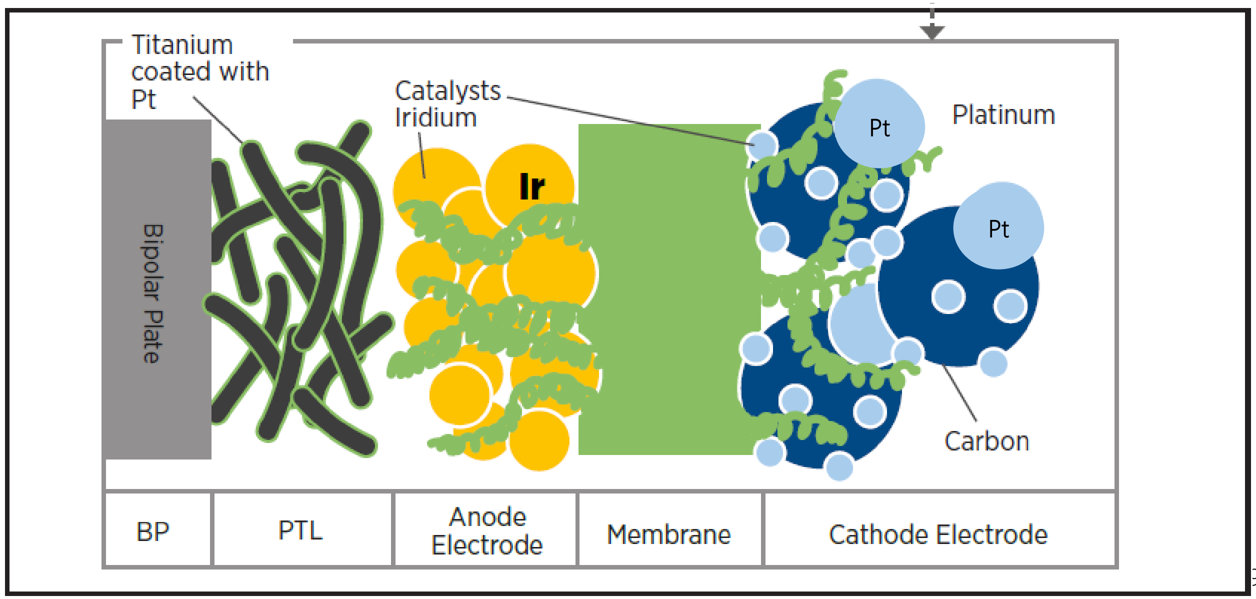
Innovation activities within PEM Electrolyzers

– can PEM components be an inspiration???

E. Taibi, IRENA, 2020.



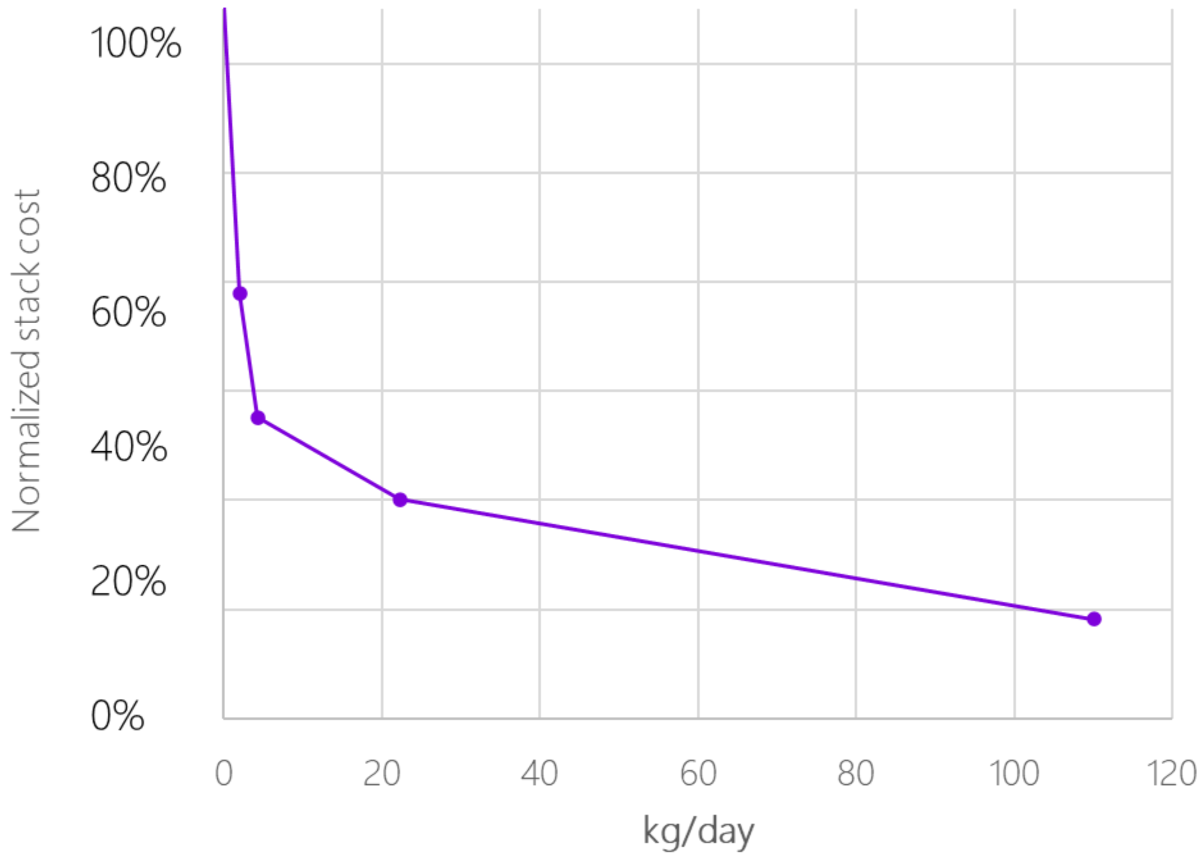
CELL LEVEL



- Demonstrated cost evolution – scale

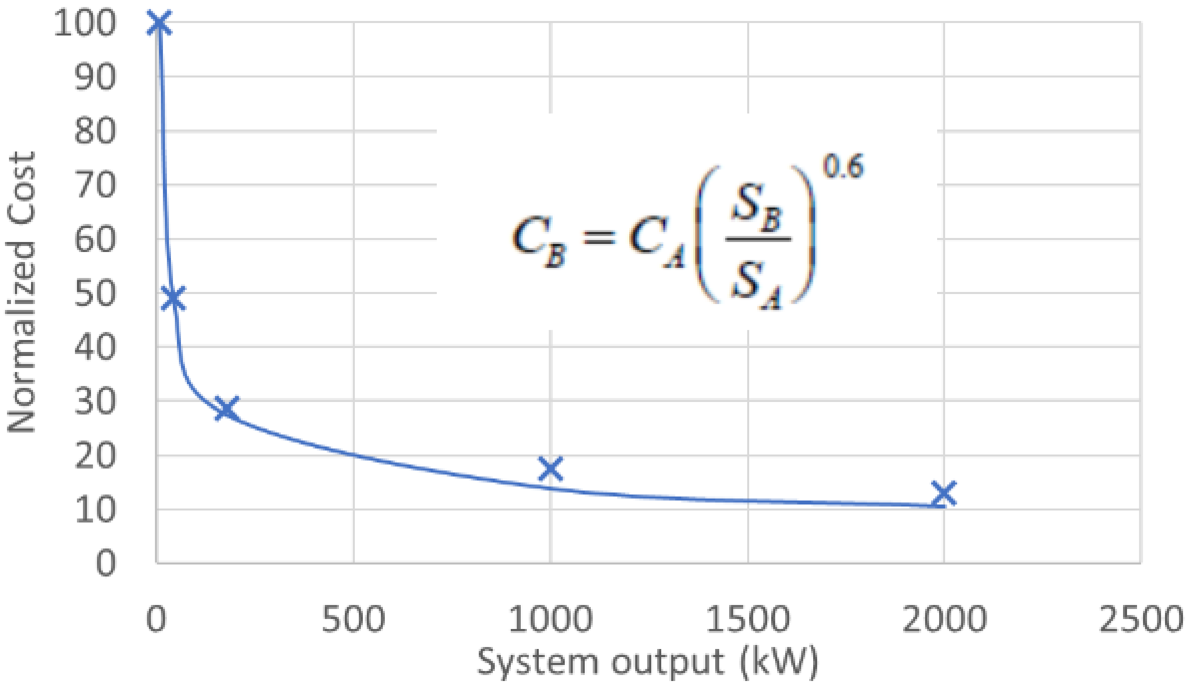
Cell Stack:

- Cost curve primarily driven by material utilization
- Improved bipolar plate format for 250 kW stack



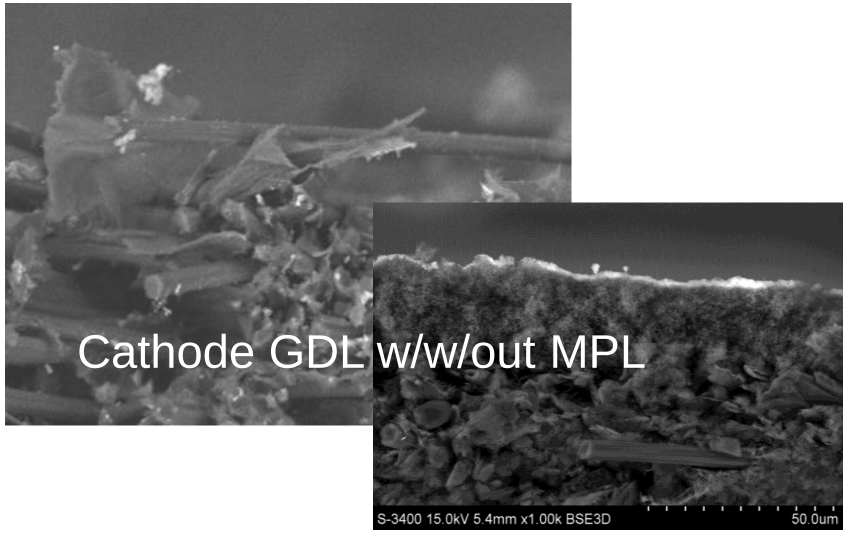
Balance of Plant:

- Rule of six tenths seems to be supported by past scale up activities

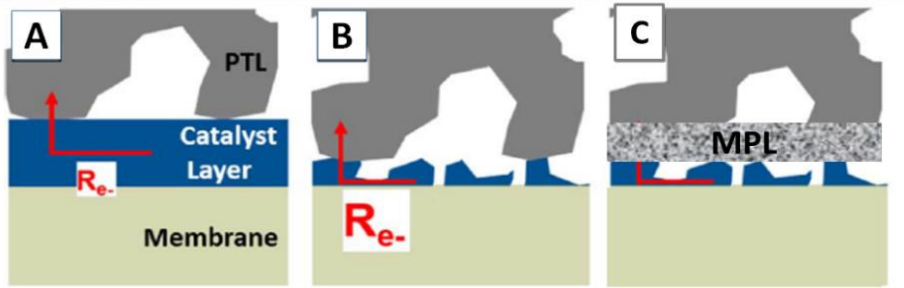


- Electrode integration: porous transport layers

- Gas diffusion layer needs to contact catalyst layer effectively while providing porosity
  - Typically involves a microporous layer (MPL) approach
  - Materials optimized for fuel cell, not electrolyzer
  - Wetproofing vs. wettability, gas vs. liquid flow
- Design and manufacturing maturity needs to catch up for electrolysis for both MEA and adjacent components

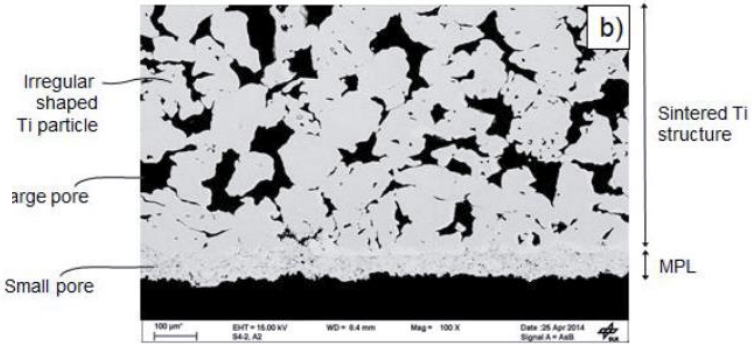


Gasteiger, ECS 2018



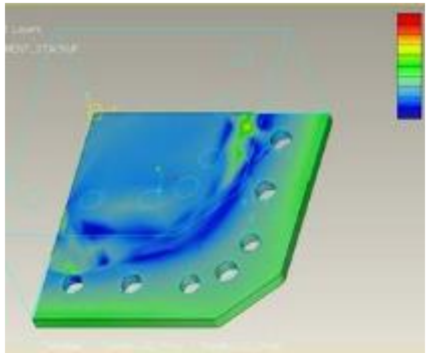
A – Thick electrode catalyst layer has lower resistance to the porous transport layer
B – Thinner electrode catalyst has very high resistance to porous transport layer
C – Microporous layer effectively contacts catalyst layer

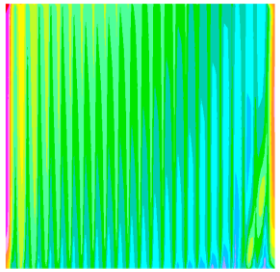
Friedrich, J. Power Sources 2016



- Example of 80% component cost reduction

Fundamental R&D to Prototyping





Component modeling

Accelerated embrittlement

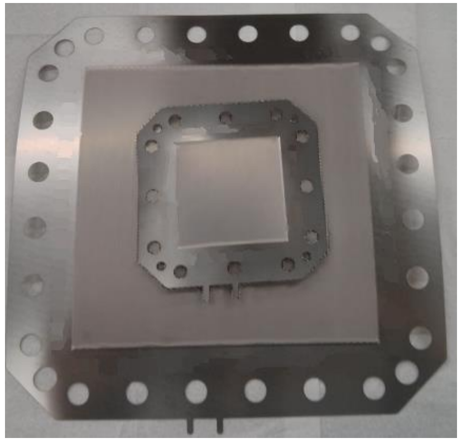
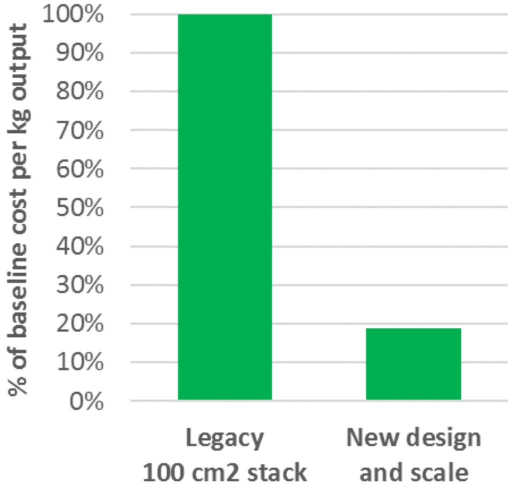
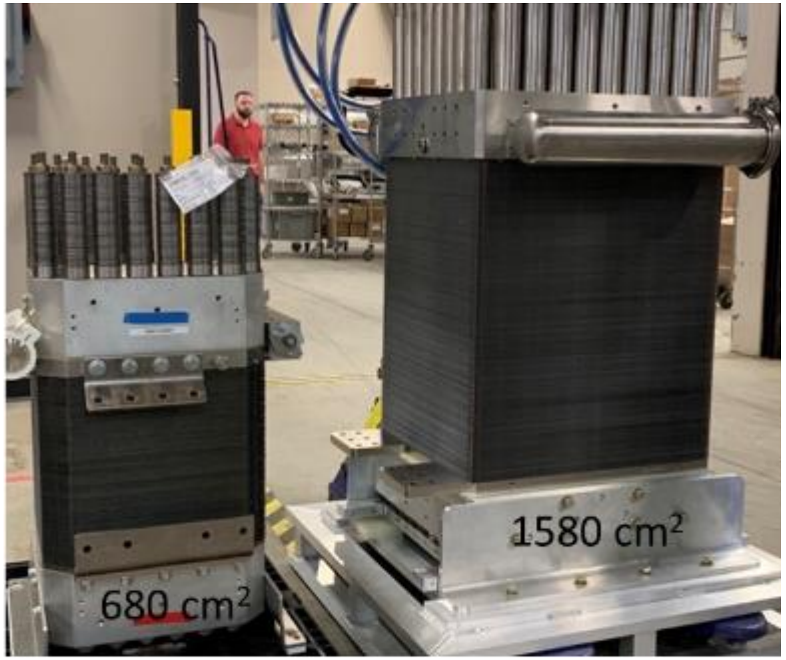


Plate manufacturing



Products from kW to MW scale

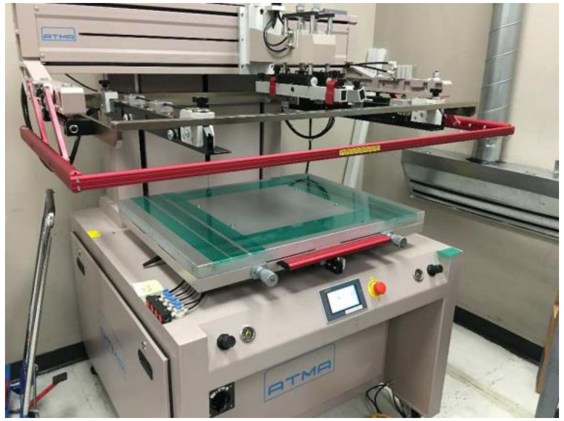
90 cm²



Nel scale up and commercialization:
MW stack based on same platform

- Example of advanced manufacturing

Roll to roll manufacturing already demonstrated for related fuel cell industry

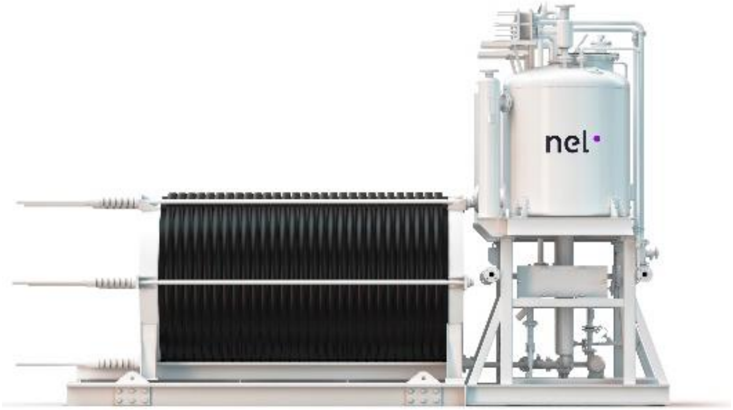


Current: T-shirt printing like
Slow, moderate control, high labor

Future: Newspaper printing like
Fast, precision, low labor

Final Remarks

– Alkaline Electrolyzers:
  - Well stablished and mature at scale technology
  - Robust
  - Low-cost



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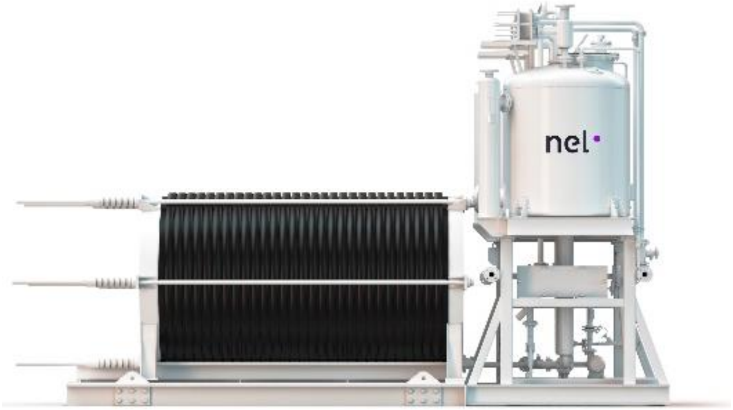

- High Potential for Innovation
  - Diaphragms
  - Electrodes
  - Porous Transport Layers and interfaces
  - Cell and Stack design for high pressure operation

Final Remarks

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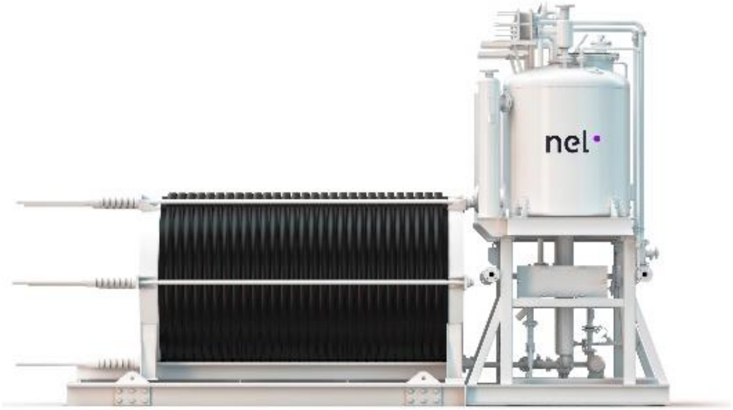

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  - Diaphragms
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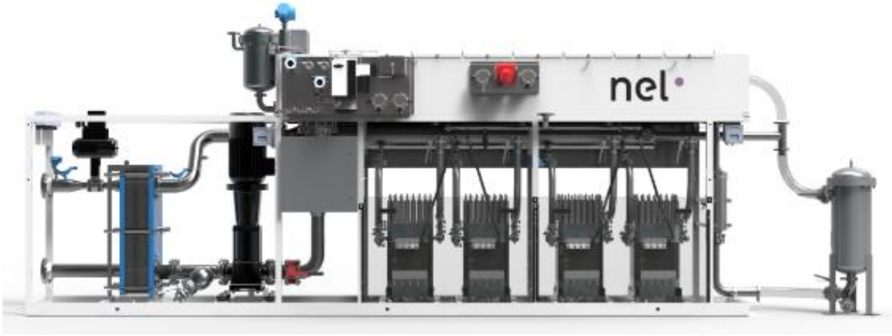
- PEM Electrolyzers
  - Significant achievements in cost and efficiency levels
  - Important steps towards automations (as with Fuel Cells, batteries) are on the making



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NEL Hydrogen:
Kathy Ayers
Egil Rasten
Everett Anderson

and you for the attention!!!

number one by nature

TRANSPORTATION

Heavy duty H_2 vehicles may be earliest market growth

- More synergistic with heavy transport vehicles like buses and shipping trucks – long range, fast fueling
- Fixed routes keep capacity high
- Larger stations reduce production cost

Photos from Hyundai website; SARTA website