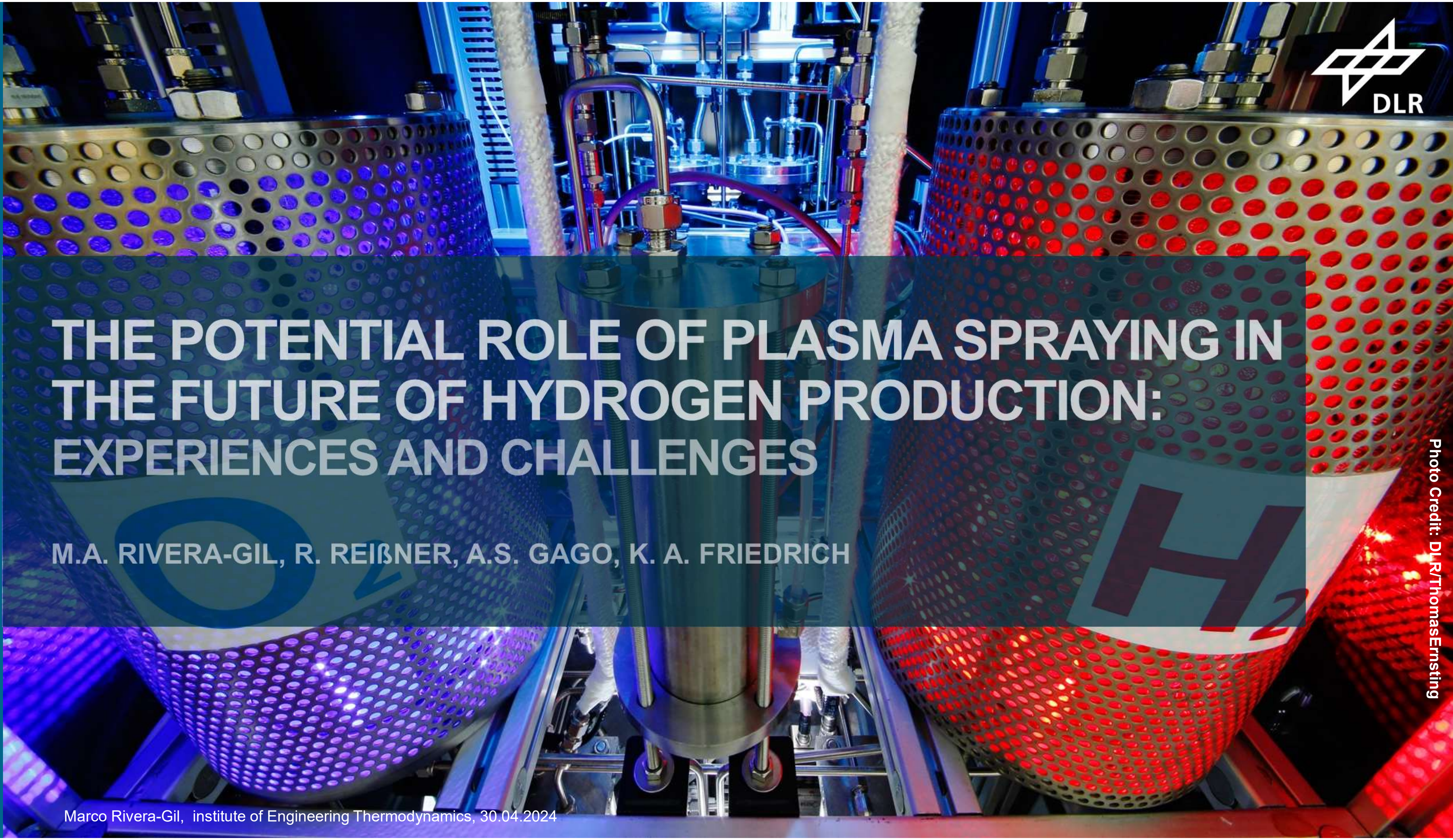


THE POTENTIAL ROLE OF PLASMA SPRAYING IN THE FUTURE OF HYDROGEN PRODUCTION:
EXPERIENCES AND CHALLENGES

M.A. RIVERA-GIL, R. REIßNER, A.S. GAGO, K. A. FRIEDRICH

Photo Credit: DLR/ThomasErnsting

Outline

1. Introduction.

2. **Motivation for water electrolysis development**

3. Experiences on the development of plasma sprayed functional coatings for alkaline water electrolysis.

4. Challenges of plasma spraying on the field of water electrolysis

German Aerospace Center (DLR)

Deutsches Zentrum für Luft- und Raumfahrt

- 30 locations in Germany
- International offices

Stuttgart Location *Dr. Anke Kovar*

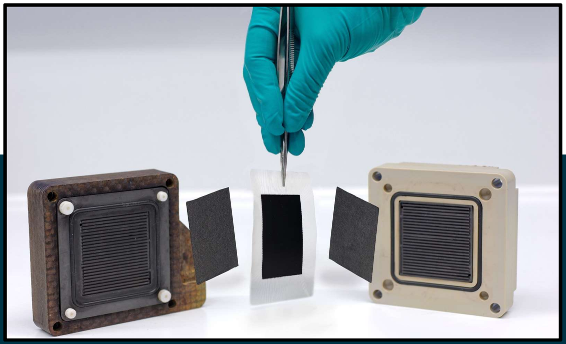
Institute of Engineering Thermodynamics

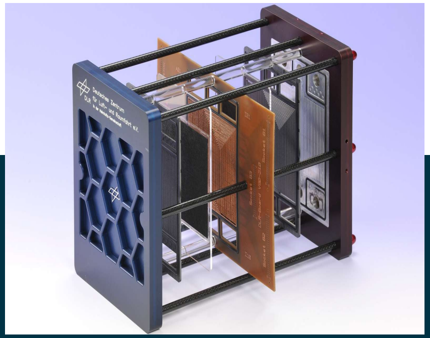
Prof. Dr. André Thess

Department of Electrochemical Energy Technology

Prof. Dr. Andreas K .Friedrich

Water Electrolysis Fuel Cells Batteries





DLR

Research fields:

- Aeronautics
- Space
- **Energy**
- Transport
- Security
- Digitalization

Motivation

Greenhouse Effect and Global Warming

Photo Credit: 1972. © NASA

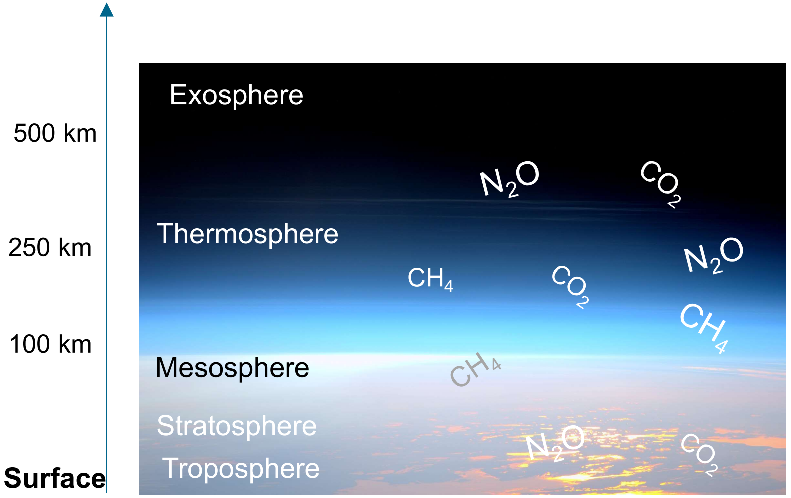
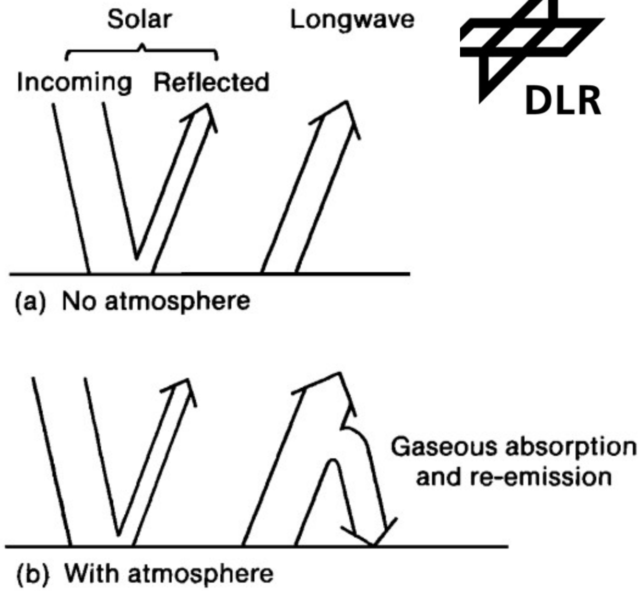


Photo Credit: DLR.de, : DLR (CC BY-NC-ND 3.0)



Mitchell, J. F. (1989). The “greenhouse” effect and climate change. Reviews of Geophysics, 27(1), 115-139.

Natural greenhouse effect

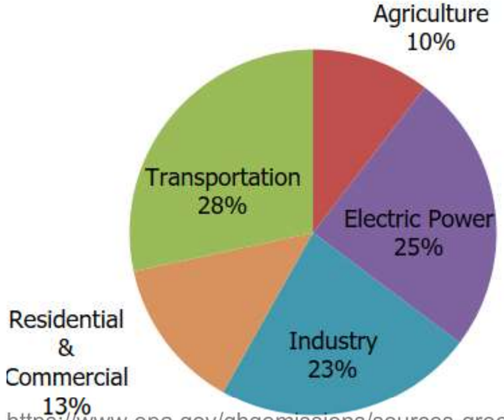
↑

CO_2 (Carbon dioxide)
CH_4 (Methane)
N_2O (Nitrous Oxide)

Anthropogenic greenhouse gases (GHG)

Hydrofluorocarbons (HFC; PFCs)
Sulphur hexafluoride (SF_6)
Nitrogen trifluoride (NF_3)

GHG Emission per sector



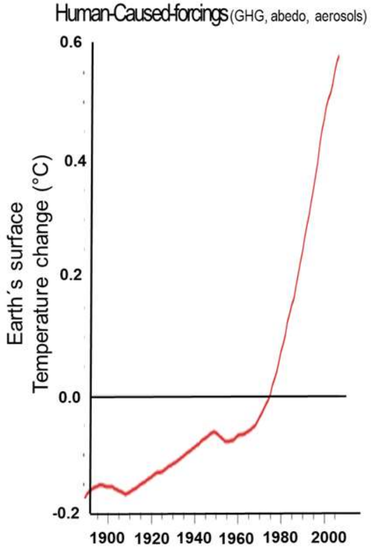
https://www.epa.gov/ghgemissions/sources-greenhouse-gas-emissions

20th century alone, global temperature has increased more than it had in the last 11,000 years !

Motivation

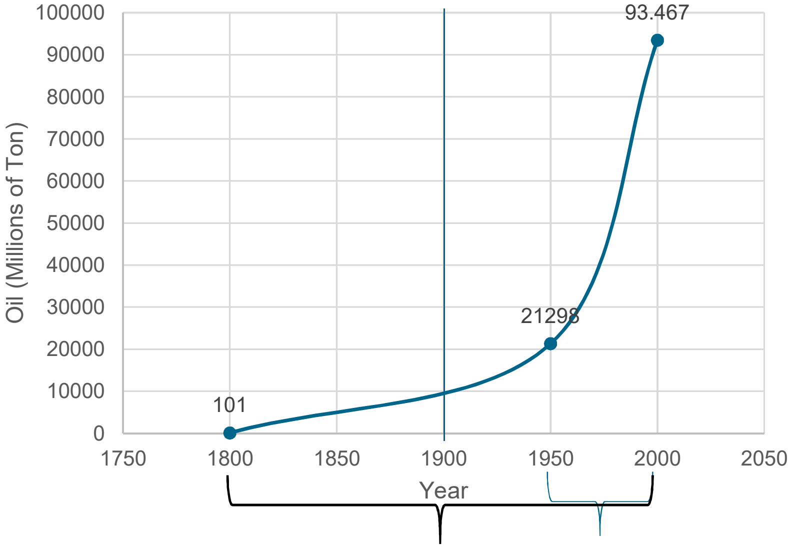
Current dependence on fossil fuels

Global Warming



Adapted from NASA Observatory

Oil consumption



92,542% Increase 439% increase

Oil and derivatives

Natural gas (Methane)

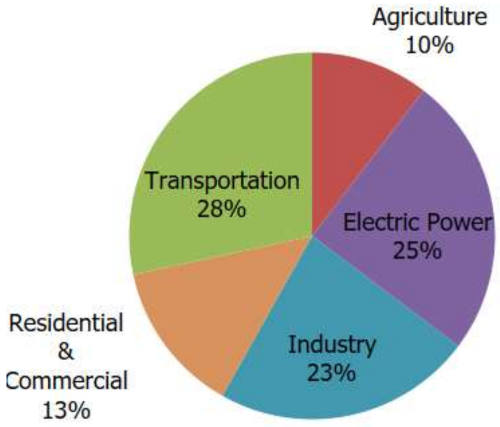
Coal

$\mathbf{CH_4} + 2O_2 \rightarrow CO_2 + 2H_2O$

Jet A – Aircraft fuel (C9–C16)

FRA ←→JFK
1,9 Ton CO_2 (Economy)
9,1 Ton CO_2 (First)

https://co2.myclimate.org/



https://www.epa.gov/ghgemissions/sources-greenhouse-gas-emissions

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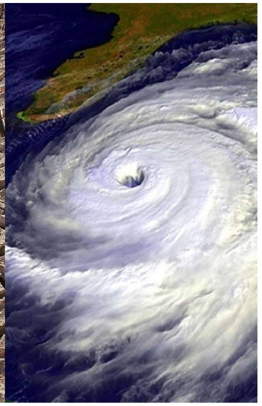
Mike McMillan/USFS

Tomas Castelazo
Wikimedia Commons



CC BY-SA 4.0, NASA.

Motivation **Hydrogen**

Most industrial sectors and human activities relate to fossil fuels

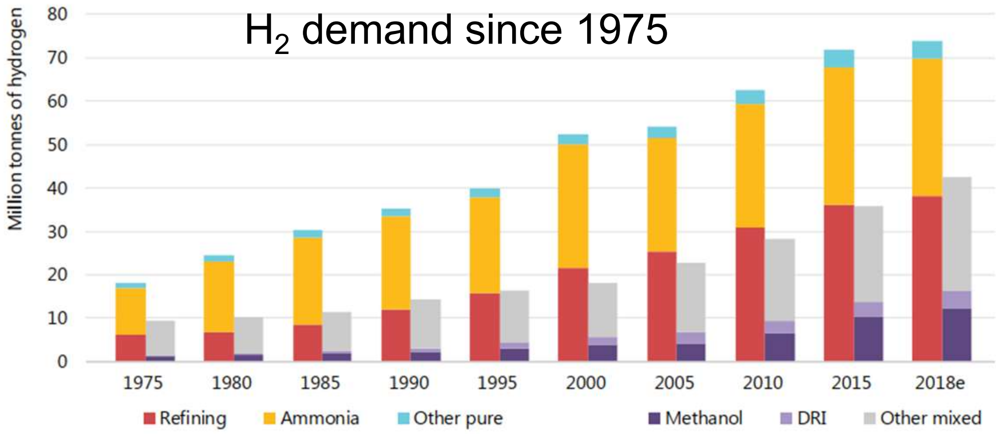
Most energy and useful work used in human activities rely on the **combustion** of fossil fuels

Fossil fuel economy

Alternative Fuels?

Hydrogen, H_2 chemical

70 million ton per year (MtH_2/yr)



H_2 demand since 1975

International Energy Agency, CC BY 4.0 DEED

Hydrogen H_2 as a fuel:

- Light
- Storable
- Reactive
- High energy content
- No green house gases emissions

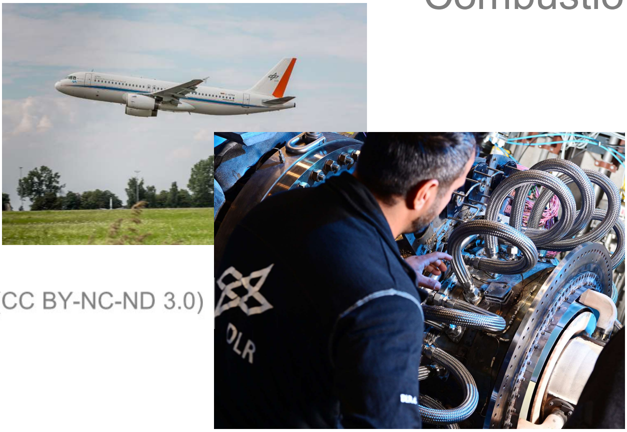
$$\mathbf{2H_2} + O_2 \rightarrow 2H_2O$$

Motivation **Hydrogen**

Hydrogen H_2 as a fuel:

$\mathbf{2H_2} + O_2 \rightarrow 2H_2O$

Combustion



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Hydrogen H_2 as energy carrier $\mathbf{2H_2} + O_2 \rightarrow 2H_2O$

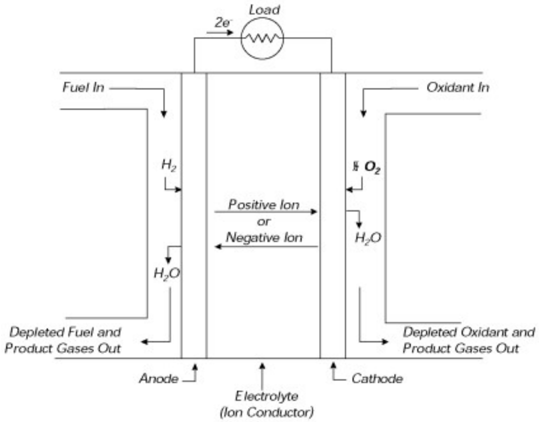
Direct transformation into electricity

Fuel cells

Electrification

$\mathbf{2H_2} \rightarrow 4H^+ + 4e$

$O_2 + 4e \rightarrow 2O^{2-}$



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DLR (CC BY-NC-ND 3.0)

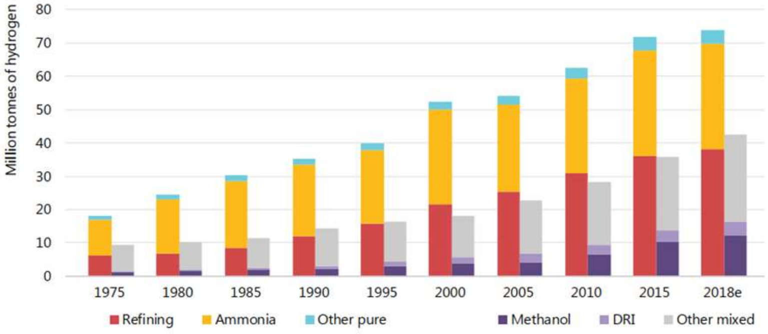
Motivation

Hydrogen Economy

Hydrogen as a fuel
Combustion
Hydrogen as energy carrier
Electrification

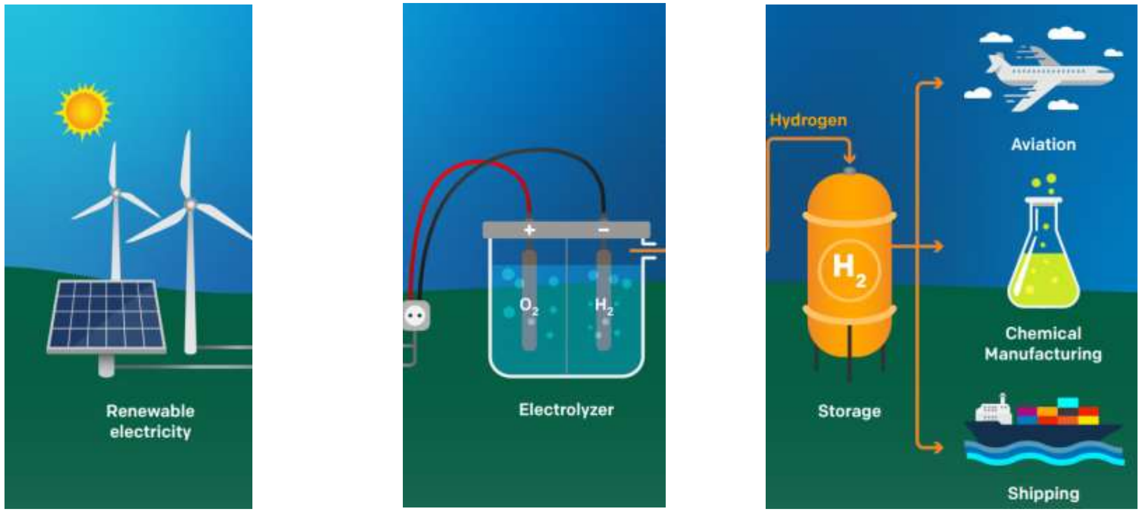
Close to zero net CO_2 emissions
Close to zero pollutants

$2H_2 + O_2 \rightarrow 2H_2O$



International Energy Agency, CC BY 4.0 DEED

Replacement for fossil fuels



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Renewables
- Photovoltaic
- Eolic

➡ Electrical Surplus/Shortages

Water electrolysis

$2H_2O \rightarrow 2H_2 + O_2$

Current demand

70 million tonnes of hydrogen/year (MtH_2)

205 billion m^3 of natural gas
(6% of global natural gas use)

1 Ton H_2 $\longrightarrow$ 10 Ton CO_2

830 Million Ton CO_2/year

Alternative Source for H_2?

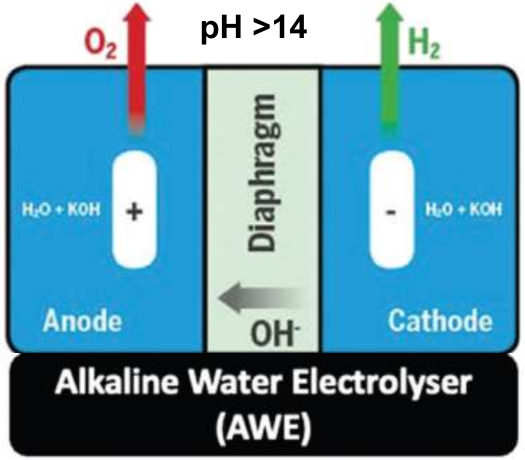
Water

Motivation

Water Electrolysis direct electrochemical reaction

$2H_2O \rightarrow 2H_2 + O_2$

Electrochemical Cell



pH >14

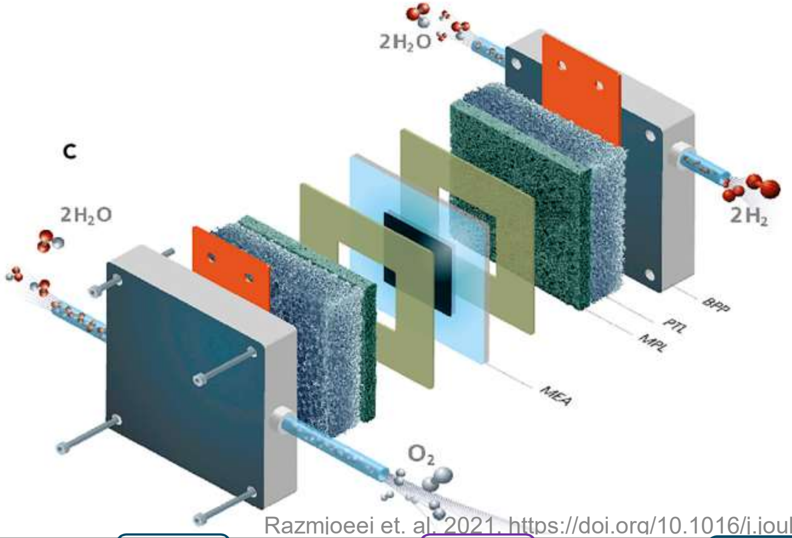
1. **Electrolyte**
2. Cathode (HER)
3. Anode (OER)

$KOH \rightarrow K^+_{(aq)} + OH^-_{(aq)}$

$\mathbf{2H_2O+2e^-} \rightarrow H_2+2OH^-$

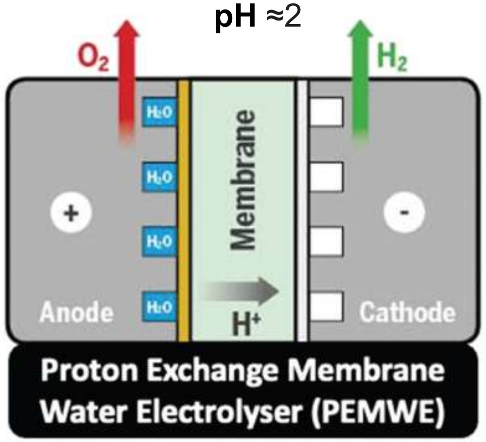
$2OH^- \rightarrow ½O_2 + H_2O + 2e^-$

$2H_2O \rightarrow 2H_2 + O_2$

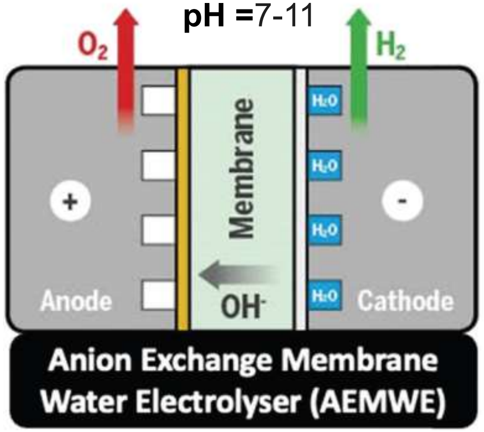


Razmjoeei et. al. 2021, https://doi.org/10.1016/j.joule.2021.05.006

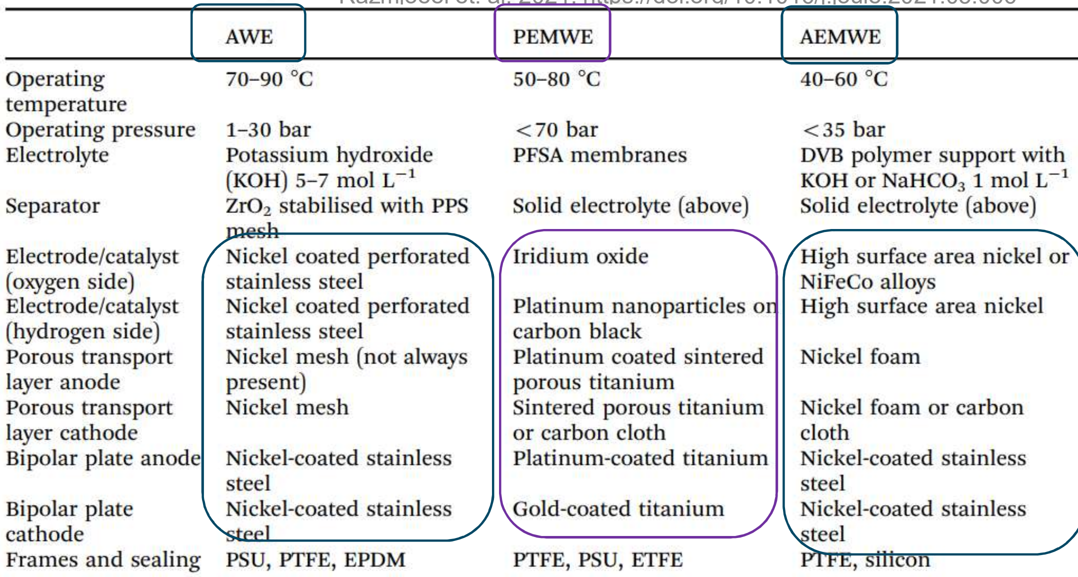
pH ≈2



pH =7-11



Chatenet et al. Chem. Soc. Rev., 2022, 51, 4583

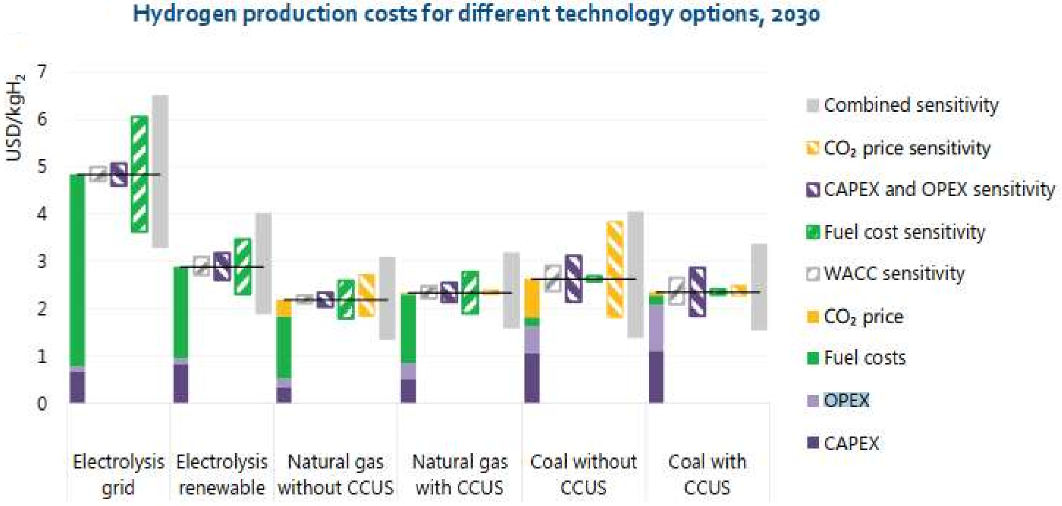


	AWE	PEMWE	AEMWE
Operating temperature	70–90 °C	50–80 °C	40–60 °C
Operating pressure	1–30 bar	<70 bar	<35 bar
Electrolyte	Potassium hydroxide (KOH) 5–7 mol L^{-1}	PFSA membranes	DVB polymer support with KOH or $NaHCO_3$ 1 mol L^{-1}
Separator	ZrO_2 stabilised with PPS mesh	Solid electrolyte (above)	Solid electrolyte (above)
Electrode/catalyst (oxygen side)	Nickel coated perforated stainless steel	Iridium oxide	High surface area nickel or NiFeCo alloys
Electrode/catalyst (hydrogen side)	Nickel coated perforated stainless steel	Platinum nanoparticles on carbon black	High surface area nickel
Porous transport layer anode	Nickel mesh (not always present)	Platinum coated sintered porous titanium	Nickel foam
Porous transport layer cathode	Nickel mesh	Sintered porous titanium or carbon cloth	Nickel foam or carbon cloth
Bipolar plate anode	Nickel-coated stainless steel	Platinum-coated titanium	Nickel-coated stainless steel
Bipolar plate cathode	Nickel-coated stainless steel	Gold-coated titanium	Nickel-coated stainless steel
Frames and sealing	PSU, PTFE, EPDM	PTFE, PSU, ETFE	PTFE, silicon

Chatenet et al. Chem. Soc. Rev., 2022, 51, 4583

Motivation **Water Electrolysis** direct electrochemical reaction

$2H_2O \rightarrow 2H_2 + O_2$

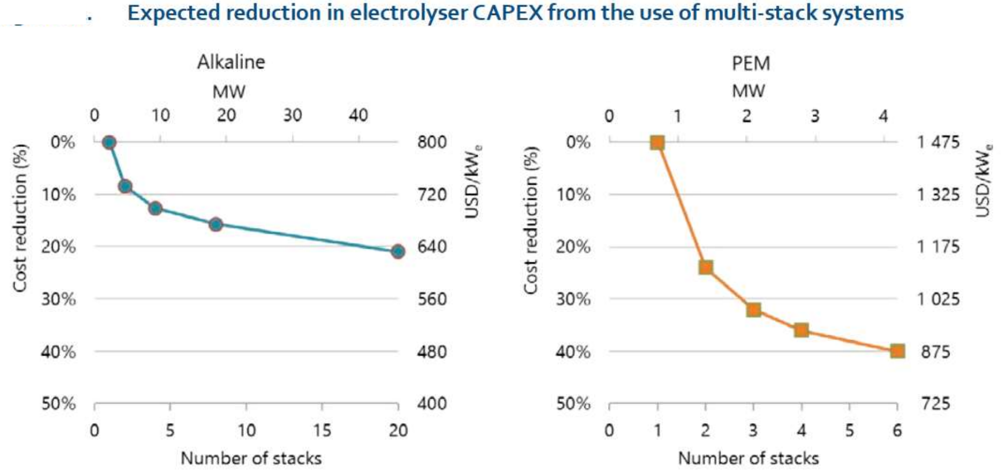

Hydrogen production costs for different technology options, 2030

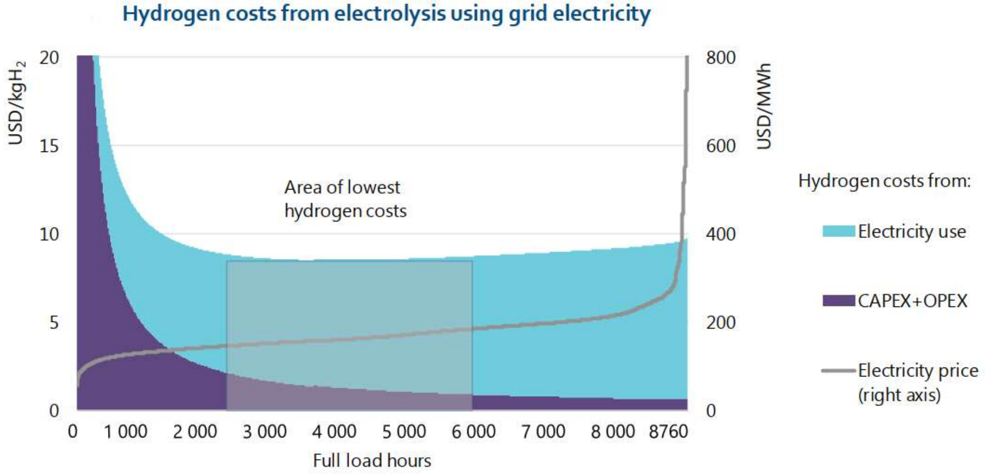
Affordability: Reduce CAPEX & OPEX

- <u>Reducing material costs</u>
- <u>Reducing fabrication costs</u>
- <u>Reducing operation and maintenance costs</u>
- <u>Increasing efficiency</u>
- <u>Increasing durability</u>

Thermal spraying?

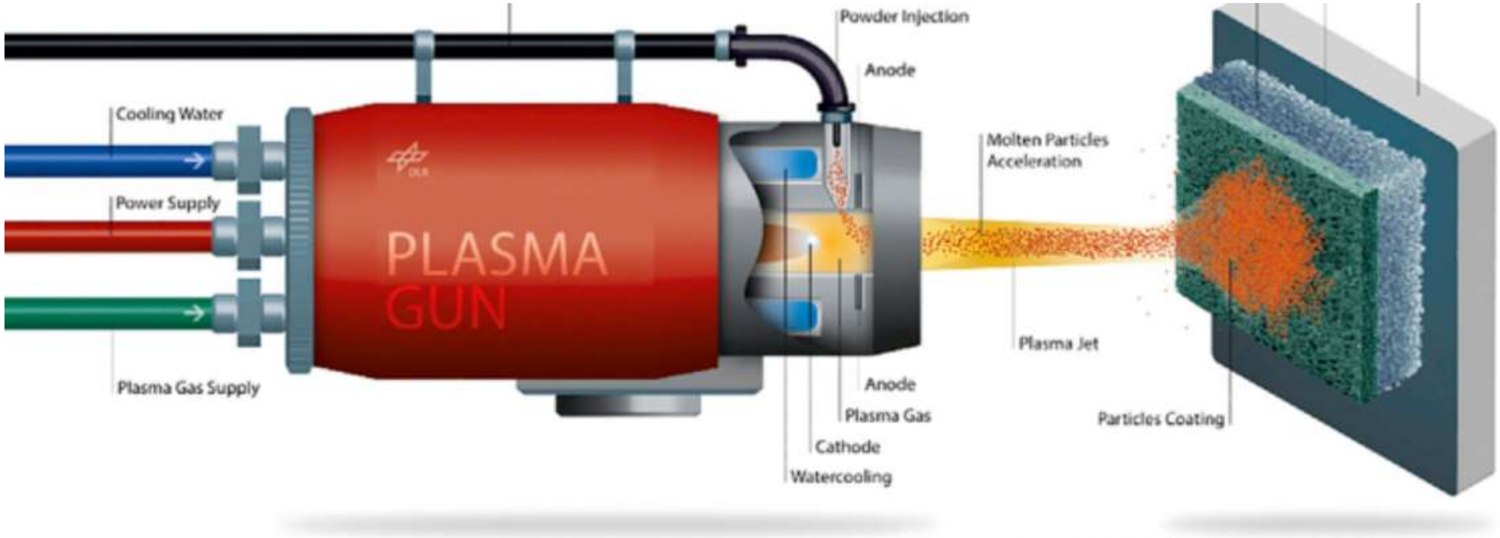
- Increasing Renewables availability


Expected reduction in electrolyser CAPEX from the use of multi-stack systems


Hydrogen costs from electrolysis using grid electricity

International Energy Agency,2019 CC BY 4.0 DEED

Experiences: **Water Electrolysis and plasma spraying**



Razmjooei et al. 2020 https://doi.org/10.1016/j.joule.2021.05.006

Thermal Spraying processes

- (Relatively) low cost
- Flexible
- Scalable
- Versatile

Control through processing parameters

- Porosity
- Thickness
- Microstructure

Experiences: **Water Electrolysis and plasma spraying (Alkaline)**

German Aerospace Center, DLR.

Schiller et al, 1995. **Vacuum Plasma Spraying** of High-Performance Electrodes for **Alkaline Water Electrolysis.** https://doi.org/10.1007/BF02646111

- **Raney** nickel **Ni-Al-Mo and Raney nickel /Co_3O_4**
- Activated coatings show **enhanced porosity**
- Coated electrodes **show better performance** than uncoated Ni
- **Unwanted phases** formed during plasma processing

Wang et al 2019. High Performance **Anion Exchange Membrane Electrolysis** Using Plasma-Sprayed, **Non-Precious-Metal** Electrodes**.** https://doi.org/10.1021/acsaem.9b01392

- Explored the applicability of **APS and VPS** for **Ni, Ni/C, and Ni-Al-Mo** coated electrodes **on SS**
- Attained **performance similar to PEMWE.**
- Durability issues require further attention.

Razmjooei et al, 2019. Highly Active Binder Free Plasma Sprayed **Non-Noble Metal** Electrodes **for Anion Exchange Membrane** Electrolysis at Different Reduced KOH Concentrations**.** doi.org/10.1149/09208.0689ecst

- APS NiAl, NiAlMo coated coponents
- **Study alternate cell configuration**
- **Investigate KOH concentration**
- Relates microstructural and structural features with plasma processing conditions

Experiences: Water Electrolysis and plasma spraying (Alkaline)

German Aerospace Center, DLR.

Razmjooei et al, 2020. Improving plasma sprayed Raney-type **nickel–molybdenum** electrodes towards high-performance hydrogen evolution in **alkaline medium**. https://doi.org/10.1038/s41598-020-67954-y

- APS NiAl, NiAlMo coated components
- Study the **influence of** total **gas flow and** plasma **power**
- Observations regarding structural, microstructural and chemical changes
- Implementation of **in/situ particle monitoring**
- **Correlation of processing** parameters **and coating** characteristics **with performance** and durability

Razmjooei et al. 2020. Increasing the performance of an **anion exchange membrane** electrolyzer operating in pure water with a nickel-based microporous layer. https://doi.org/10.1016/j.joule.2021.05.006

- Studied **Ni-C APS coatings** for MPL
- Novel approach to cell configuration with multifunctional liquid gas diffusion layers
- **Operation of AEMWE with pure water**
- Analysis and **correlation** of **porosity** and **processing** parameters with **cell performance**

Experiences: Water Electrolysis and plasma spraying (Alkaline)

Universite de Sherbrooke, Canada

Birry and Lasia 2004,. Studies of the hydrogen evolution reaction on Raney nickel–molybdenum electrodes https://doi.org/10.1023/B:JACH.0000031161.26544.6a

- **Alkaline water Electrolysis**
- Use of **VPS** to produce NiAlMo coated electrodes
- Study of **different Ni/Al/Mo composition** in the plasma feedstock
- NiAlMo coated electrodes show better performance than corresponding bulk materials
- **No observations regarding structural or microstructural characteristics**

University of Strathclyde, UK

Chade et al. 2013. Evaluation of Raney nickel electrodes prepared **by atmospheric plasma spraying** for **alkaline water electrolysers** https://doi.org/10.1016/j.joule.2021.05.006

- NiAl coated electrodes
- **Study of the thickness'** influence in the performance of AWE
- **No cross section** or microstructural details are given

Experiences: Water Electrolysis and plasma spraying (Alkaline)

Korea Institute of Energy Research

Kim et al. 2019, Electrochemical characterization of Raney nickel electrodes prepared by **atmospheric plasma spraying** for **alkaline water electrolysis** https://doi.org/10.1016/j.jiec.2018.10.010

- Alkaline water Electrolysis
- Use of APS to produce NiAl coated electrodes
- **Proposes H_2 reduction method to leach remnant**
- Does not provide discussion around processing parameters or microstructure

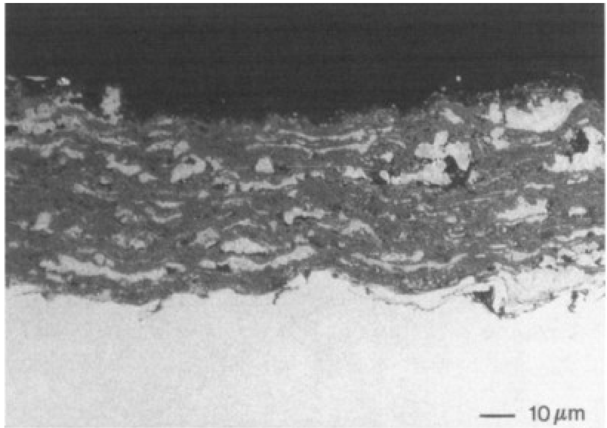
Guangxi University of Science & Technology, China

Liang et al. 2020. Preparation of NiAl coated Nickel foam cathode for **Alkaline Water Electrolysis using Atmospheric Plasma Spraying** https://doi.org/10.20964/2020.06.61

- NiAl coated electrodes
- Study the performance of **APS coatings on Ni foam electrodes**
- No cross section or microstructural detail is given

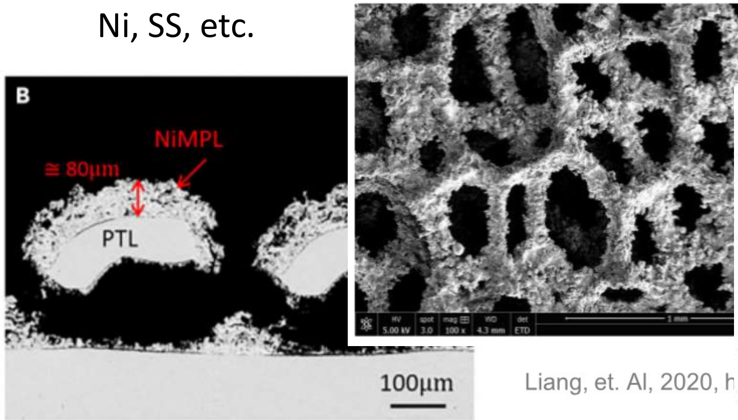
Experiences Water Electrolysis and plasma spraying (Alkaline)

Study of different feedstock materials
Ni, Ni-C, NiAlMo, Co_3O_4



Schiller et. al. 1995. https://doi.org/10.1007/BF02646111

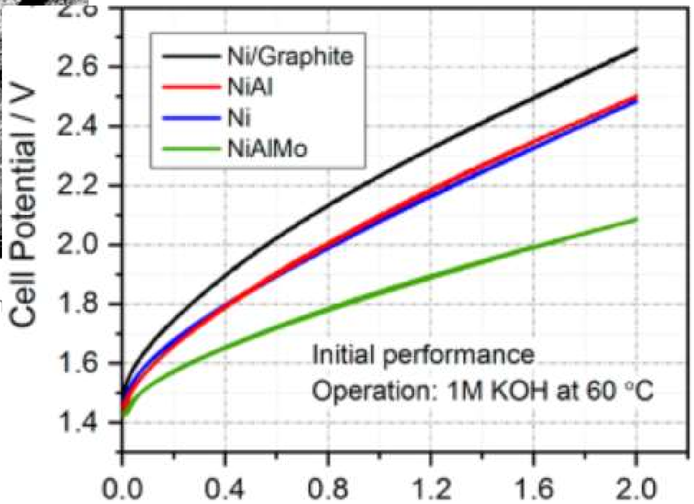
Study of different substrates (base llectrodes)
Ni, SS, etc.



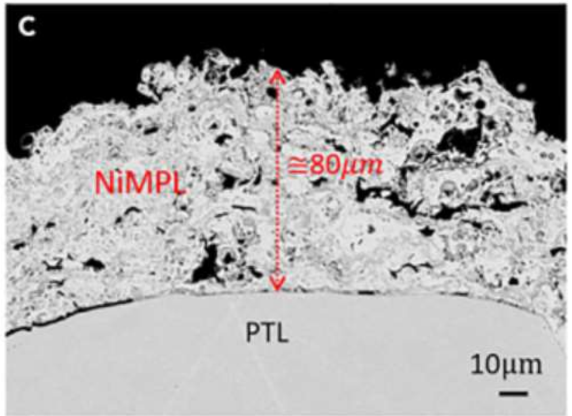
Liang, et. Al, 2020, h

azmjooei et al. 2020 https://doi.org/10.1016/j.joule.2021.05.006

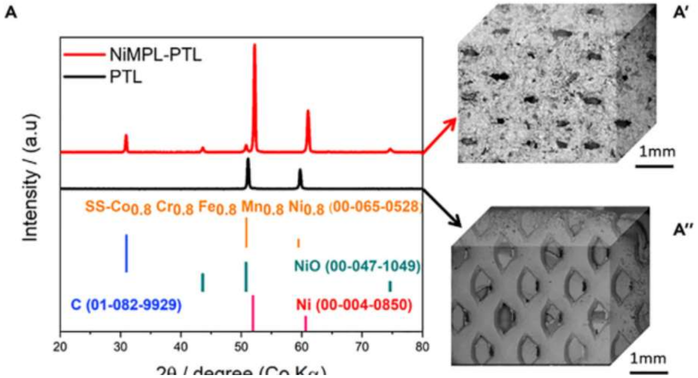
Performance



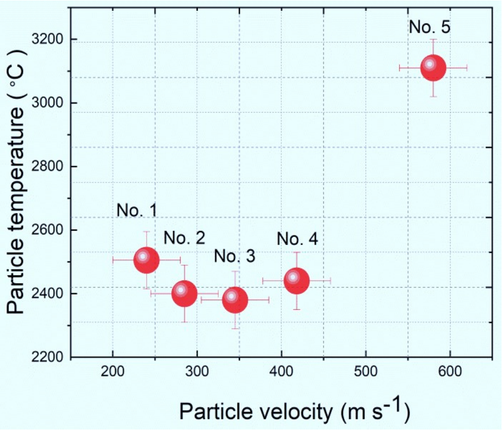
Thickness



Porosity and phase transformation



Particle Diagnostics



Experiences Water Electrolysis and thermal spraying

Plasma spraying (APS, and VPS) is a suitable and effective process to produce low cost components for water electrolysis

- Alkaline Water Electrolysis
- Anion Exchange Membrane Water Electrolysis

German Aerospace Center, DLR
Korea Institute of Energy Research
University of Strathclyde, UK
Universite de Sherbrooke, Canada
Guangxi University of Science & Technology, China

Thermal spraying (APS, VPS, HVOF, HVAF and CGS) is a suitable and effective family of process to produce low cost components for proton exchange membrane water electrolysis **PEMWE.**

- German Aerospace Center. APS and VPS
- RWTH Aachen, Germany . CGS, HVAF and HVOF ITSC 2024 abstract 7905, 29.04.2024
- RWTH Aachen, Germany, HVOF, abstract 7909, 30.04.2024

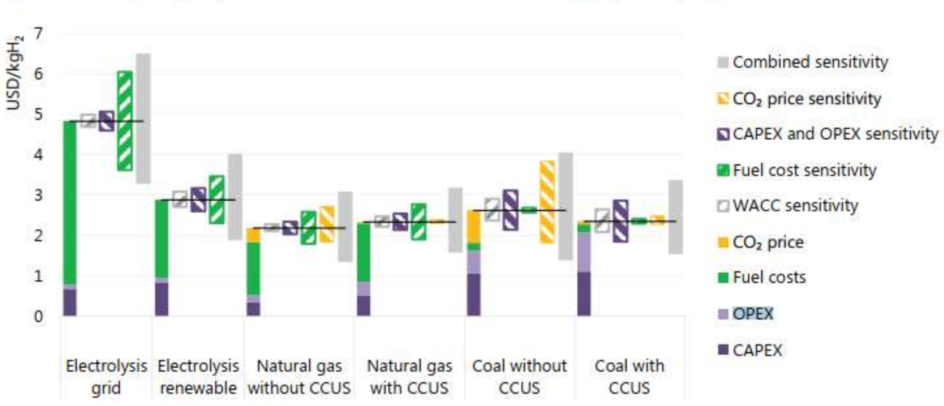
Challenges

Water Electrolysis

Some WE challenges

- Increase Efficiency.
- Increase durability.
- Increase reliability.
- Decrease CAPEX/OPEX.
- Decrease dependence of critical raw materials (e.g. Ir, Rd, Pt).
- Increase H_2 production capacity.
- Integration with renewables.
- Others

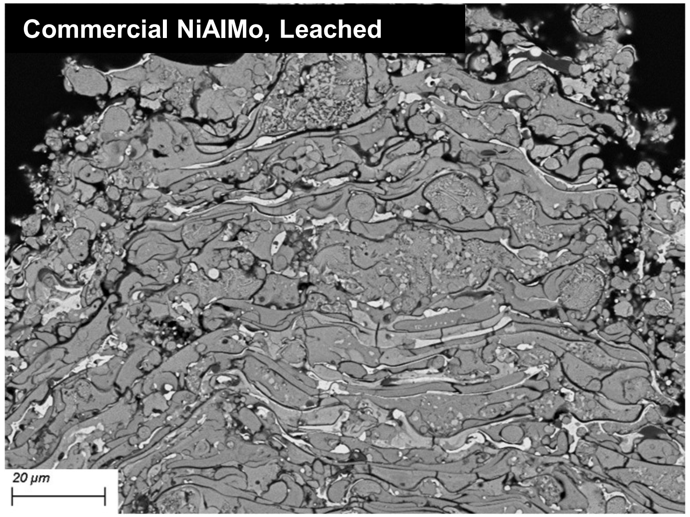
Hydrogen production costs for different technology options, 2030



International Energy Agency,2019 CC BY 4.0 DEED

Thermal spraying

- Increased and controlled open porosity.
- Control of phase transformation.
- Increase durability (e.g. mechanical properties)
- Develop effective, cost affordable and flexible processes.



DLR (CC BY-NC-ND 3.0)

- ❖ Inherent porosity of thermal-sprayed coatings
- ❖ Compromise of process temperature with phase transformation
- ❖ Compromise of porosity with mechanical characteristics

Thank you for your attention!

German Aerospace Center
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Institute of Engineering Thermodynamics
Department of Electrochemical Energy Technology

http://www.DLR.de