Zero-gap water electrolysers for storing electricity: current status and perspectives

Foteini Sapountzi

syngaschem BV
synthesis gas chemistry
fundamental research projects
www.syngaschem.com

DIFFER
Dutch Institute for Fundamental Energy Research

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Catalytic Surface Science, Electrochemistry Research

- Director: Prof J W Niemantsverdriet
- Deputy Director: Dr C J Weststrate
- 2 Research Scientists
  Dr H Fredriksson, Dr F Sapountzi
- 2 PhD students: D Garcia, D Sharma
- 2 Interns: D Leurs, Y Bannink

Laboratory: SynCat@DIFFER, Eindhoven

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Syngaschem BV is research partner of Synfuels China Technology, Co Ltd

focus:

green electricity in syngas technology

electricity storage in EU – greening CTL in China

The SynCat Organisation

SynCat @ Beijing

The Synfuels China Laboratory for Fundamental Catalysis
Science & Technology for Clean Fuels from Coal

Synfuels China, Huairou, Beijing

Directors: Hans Niemantsverdriet & Yongwang Li

10 scientific staff, tech staff, students

- **Surface and Materials Science**
- **Catalysis**
- **Computational modeling**

Eindhoven: Syngaschem BV, (SynCat@DIFFER)

3 scientific staff; office manager + director

- **Fundamental Catalytic Surface Science**
- **Electrochemistry Research**

SynCat Ac@demy

for science courses and personal development

International Partners:

University of Cape Town, University of the Free State

iNano Aarhus, Cardiff Catalysis Institute

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SYNFUELS CHINA

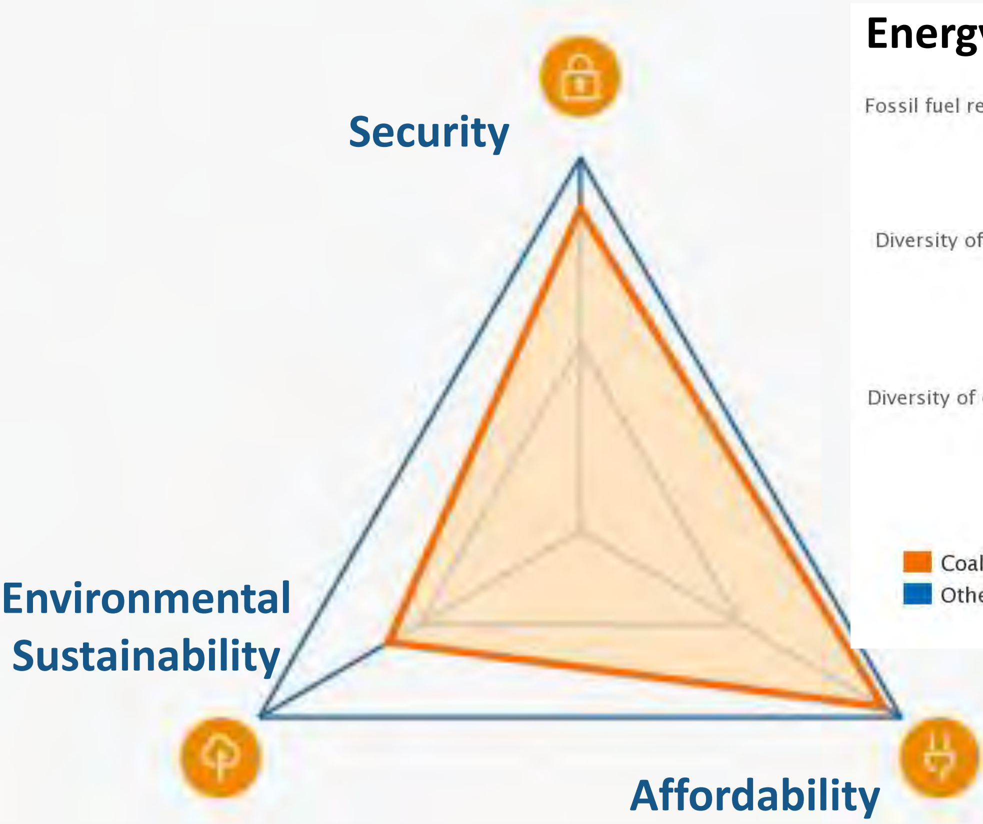
Energy trilemma index*, Netherlands 2018

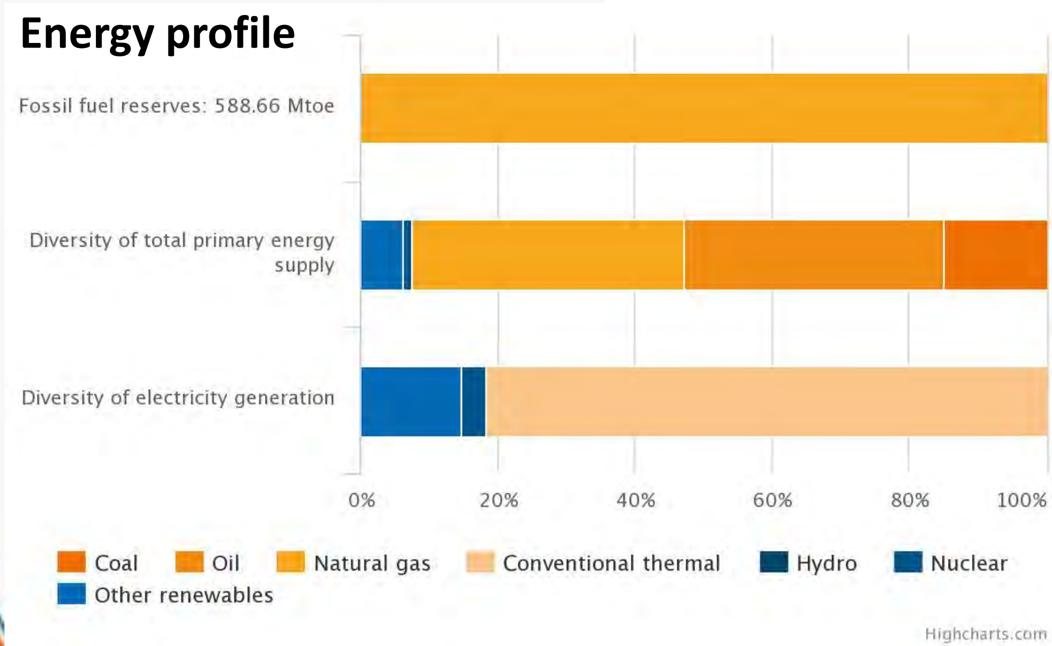
Energy Trilemma Balance, NL (2018)

Balance Score: AAB

Index Rank: 4

**Rating of how well the trade-offs of the Trilemma are managed; "AAA" is best.*





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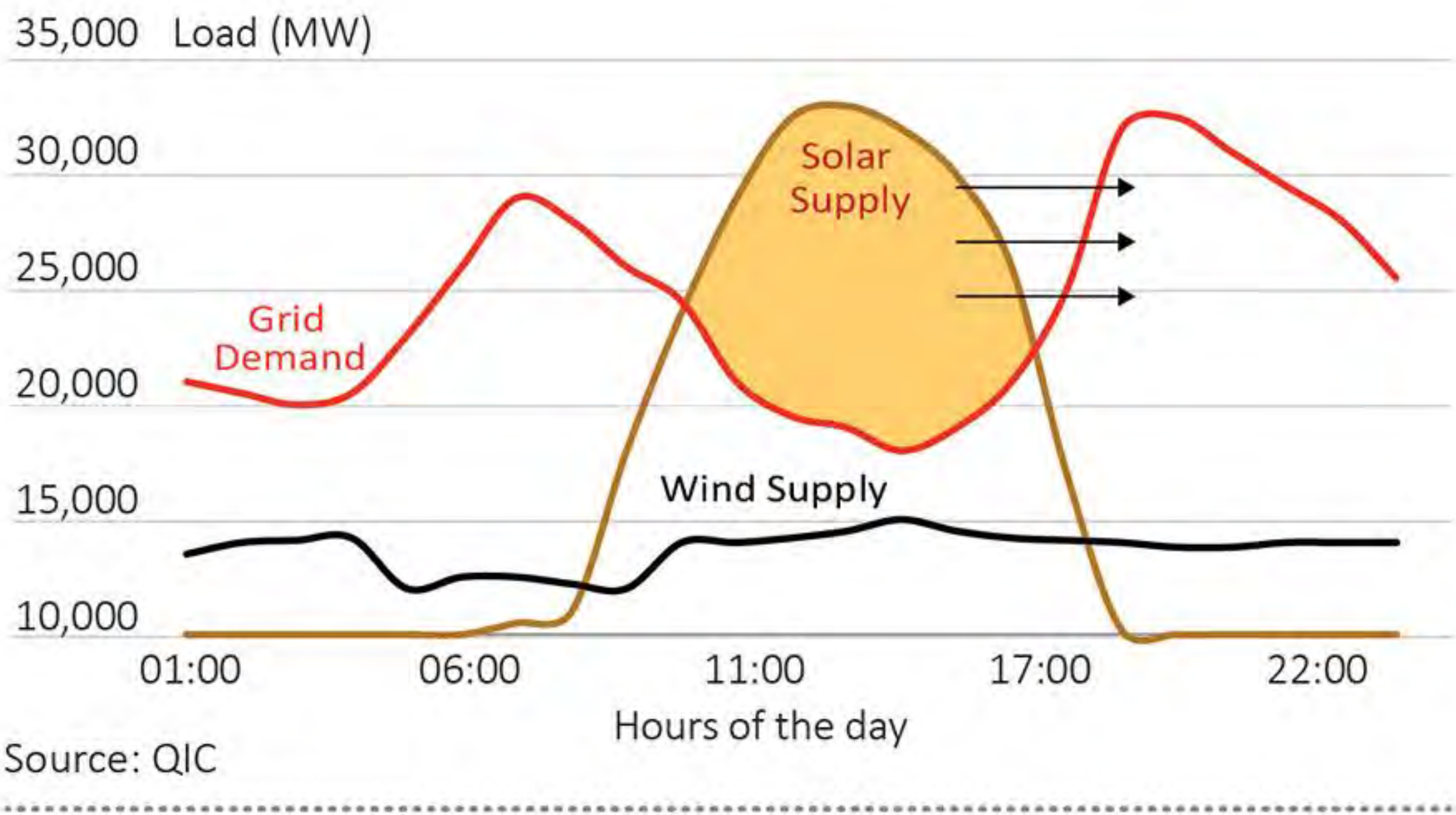
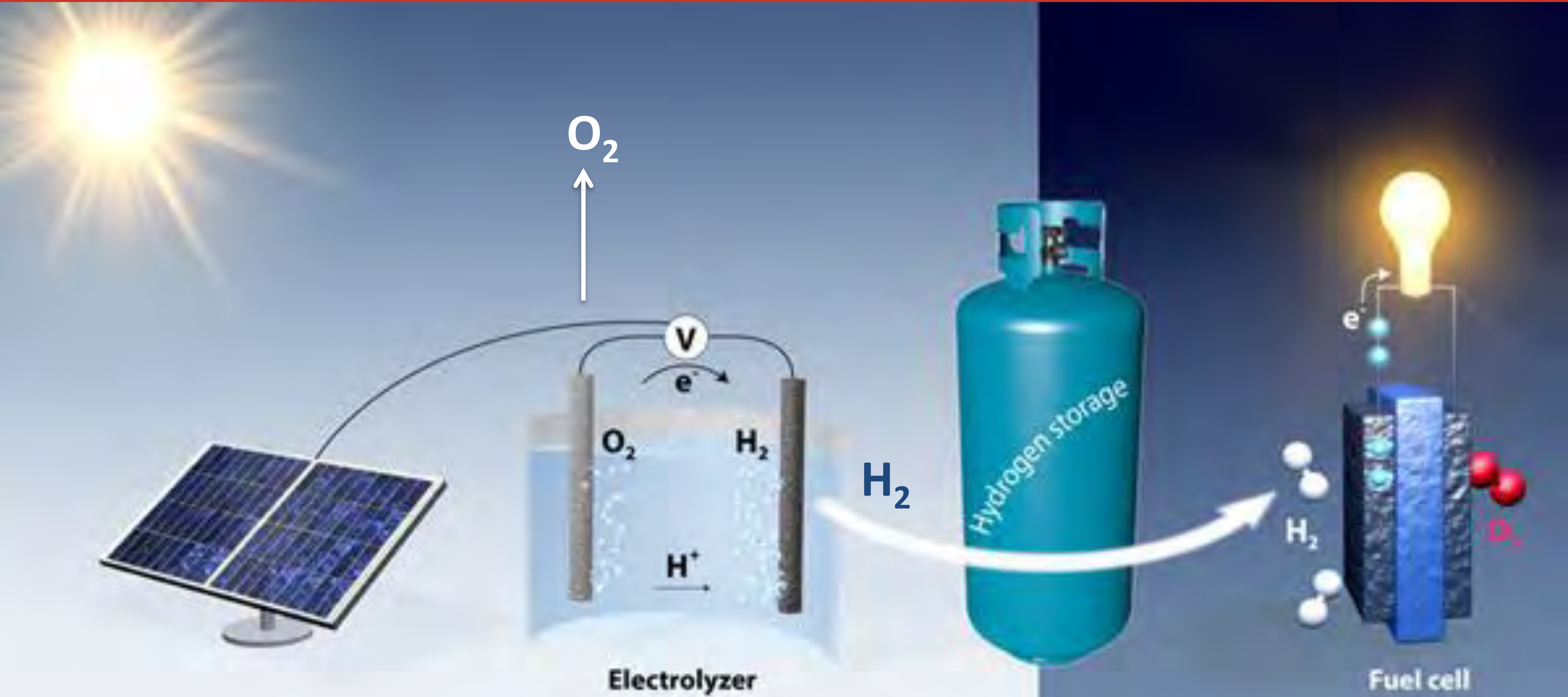
https://www.worldenergy.org/data/trilemma-index/country/netherlands/

Intermittency of Renewable Energy Sources:



Storing renewable energy is essential!

Storing energy in chemical bonds



Source: Phys.org, Chris Cesare, Stanford University, November 2014

Syngaschem BV: Storage of energy in H_2, or in synthetic fuels via synthesis gas and Fischer-Tropsch Synthesis; integration of O_2 / H_2 in coal gasification (China)

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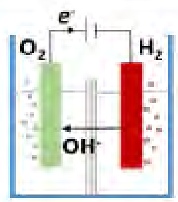
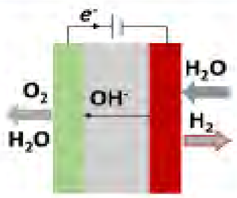
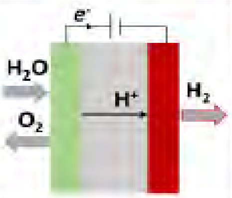
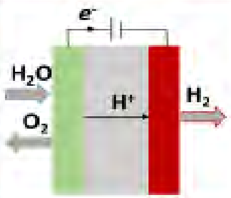
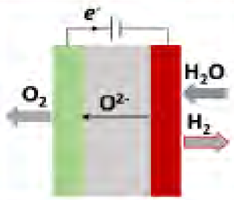
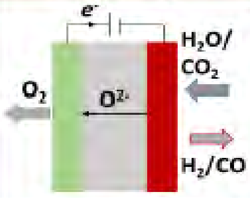
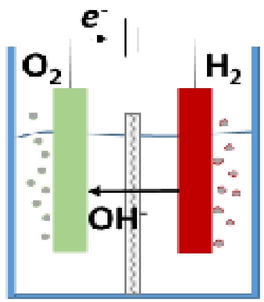
	Low temperature Electrolysis			High temperature Electrolysis		
	Alkaline (OH-) electrolysis		Proton Exchange (H^+) electrolysis		Oxygen ion (O^{2-}) electrolysis	
	Liquid	Polymer Electrolyte Membrane		Solid Oxide Electrolysis (SOE)		
	Conventional	*Solid alkaline*	*H^+ - PEM*	*H^+ - SOE*	*O^{2-} - SOE*	*co-electrolysis*
Operation principles						
Charge carrier	OH^-	OH^-	H^+	H^+	O^{2-}	O^{2-}
Temperature	20-80°C	20-80°C	20-200°C	500-1000°C	500-1000°C	750-900°C
Electrolyte	liquid	solid (polymeric)	solid (polymeric)	solid (ceramic)	solid (ceramic)	solid (ceramic)
Anodic Reaction (OER)	$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$	$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$	$2H_2O \rightarrow 4H^+ + O_2 + 4e^-$	$2H_2O \rightarrow 4H^+ + 4e^- + O_2$	$O^{2-} \rightarrow {}^1/_2 O_2 + 2e^-$	$O^{2-} \rightarrow {}^1/_2 O_2 + 2e^-$
Anode Materials	Ni>Co>Fe (oxides) Perovskites: $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, $LaCoO_3$	Ni	IrO_2, RuO_2 $Ir_xRu_{1-x}O_2$ Supports: TiO_2, ITO, TiC	Perovskites with protonic-electronic conductivity	LSM-YSZ	LSM-YSZ
Cathodic Reaction (HER)	$4H_2O + 4e^- \rightarrow 4OH^- + 2H_2$	$4H_2O + 4e^- \rightarrow 4OH^- + 2H_2$	$4H^+ + 4e^- \rightarrow 2H_2$	$4H^+ + 4e^- \rightarrow 2H_2$	$H_2O + 2e^- \rightarrow H_2 + O^{2-}$	$H_2O + 2e^- \rightarrow H_2 + O^{2-}$ $CO_2 + 2e^- \rightarrow CO + O^{2-}$
Cathode Materials	Ni alloys	$NiFe_2O_4$	Pt/C MoS_2	Ni-cermets	Ni-YSZ Substituted $LaCrO_3$	Ni-YSZ perovskites
Efficiency	59-70%		65-82%	up to 100%	up to 100%	-
Applicability	commercially available	laboratory scale	near-term commercialization	laboratory scale	laboratory scale	laboratory scale
Advantages	low capital cost, relatively stable, mature technology	combination of alkaline and H^+-PEM electrolysis	compact design, fast response/start-up, high-purity H_2	enhanced kinetics, thermodynamics: lower energy demands, low capital cost		direct production of syngas
Disadvantages	corrosive electrolyte, gas permeation through diaphragm, slow dynamics	low OH^- conductivity in polymeric membranes	high cost of polymeric membranes, acidic environment: noble metals	mechanically unstable electrodes (cracking), safety issues: improper sealing		
Challenges	Improvement in durability/reliability Enhance OER	Improvement in efficiency	Reduced noble-metal utilization	microstructural changes in the electrodes: delamination, blocking of TPBs, passivation		C deposition, microstructural changes in electrodes

F.M. Sapountzi, J.M. Gracia, C.J. Weststrate, H.O.A. Fredriksson, J.W. Niemantsverdriet, Prog. Energy Combust. Sci. 58 (2017) 1-35 (***NB: open access!!***)

Alkaline electrolysis

Operation principles	
Charge carrier	OH^-
Temperature	20-80°C
Electrolyte	liquid
Anodic Reaction (OER)	$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$
Anodes	Ni > Co > Fe (oxides) Perovskites: $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, $LaCoO_3$
Cathodic Reaction (HER)	$4H_2O + 4e^- \rightarrow 4OH^- + 2H_2$
Cathodes	Ni alloys

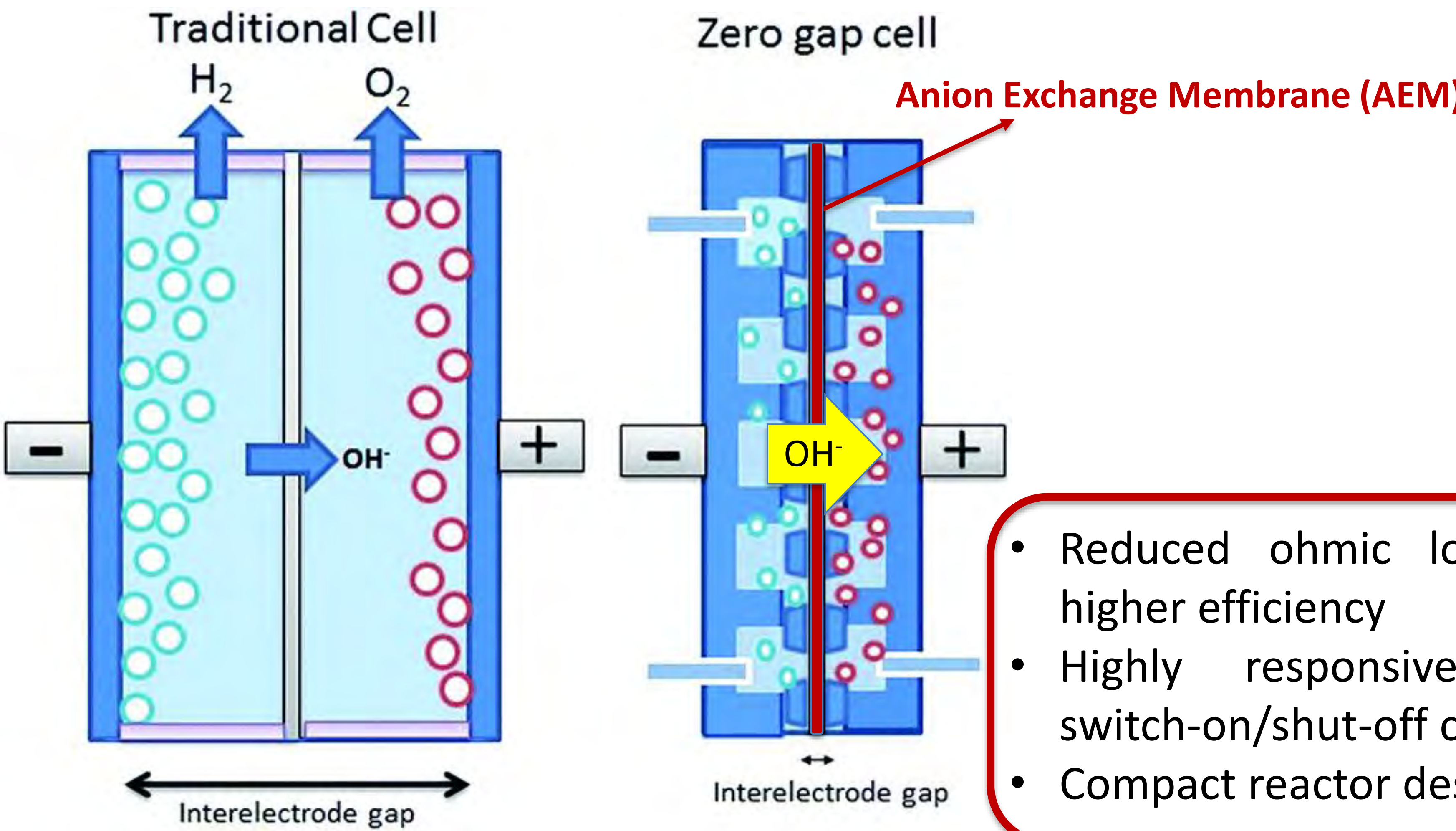
Status:

- Commercialized technology
- Low capital costs

Challenges:

- Ni-based electrocatalysts:
  trade-off between activity and cost:
  new, more active materials needed
- Based on aqueous electrolytes:
  slow response to switch-on/shut-off cycles: not ideal for coupling with intermittent energy sources

Zero-gap design: decreased intra-electrode distance



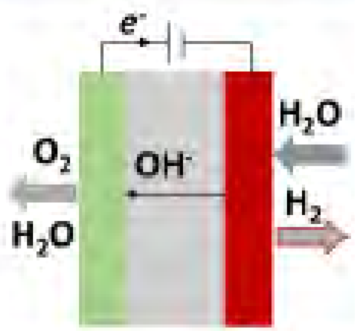
(>2 mm)

(<0.5 mm)

- Reduced ohmic losses: higher efficiency
- Highly responsive to switch-on/shut-off cycles
- Compact reactor design

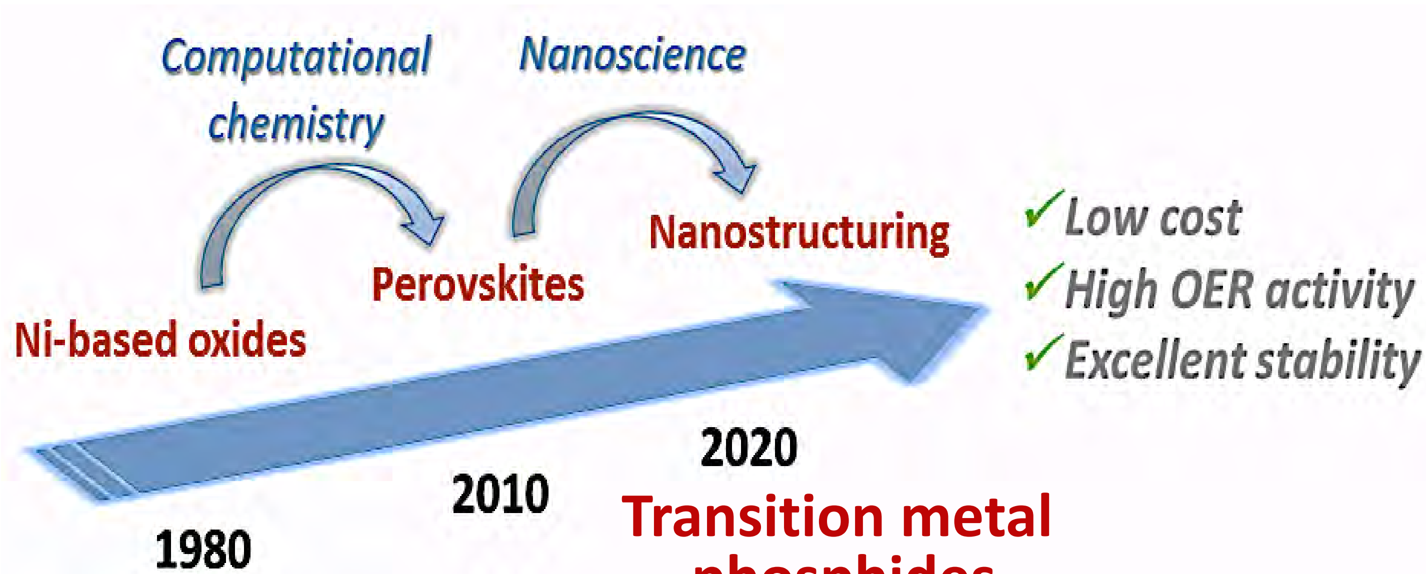
Figure from R. Phillips, C.W. Dunnill, RSC Advances 6 (2016) 100643-100651

Anion Exchange Membrane (AEM) electrolysis



OH^-
20-80°C
solid (polymeric)
$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$
Ni
$4H_2O + 4e^- \rightarrow 4OH^- + 2H_2$
$NiFe_2O_4$

- Cheap, Ni-based electrocatalysts
  (as in conventional electrolysis)
- Need for more active and stable materials

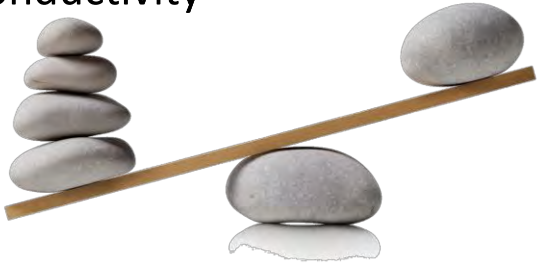


Transition metal phosphides

F.M. Sapountzi, J.M. Gracia, C.J. Weststrate, H.O.A. Fredriksson, J.W. Niemantsverdriet, Prog. Energy Combust. Sci. 58 (2017) 1-35

Anion exchange membranes

<u>The challenge:</u>



N-containing head groups	N-free head groups
Quaternary ammonium/tertiary diamines	Phosphonium
(Benz)Imidazolium	Sulphonium
Guanidinium	Metal cations
Pyridinium	

J.R. Varcoe, P. Atanassov, D.R. Hickner, P.A. Kohl, A.R. Kucernak, W.E. Mustain, K. Nijmeijer, K. Scott, T. Xuk, L. Zhuang, Energy Environ. Sci. 7 (2014) 3135-3191;
K.F.L. Hagelsteijn, S. Jiang, B.P. Ladewig, J. Mater. Sci. 53 (2018) 11131-11150

Pristine-polybenzimidazole doped with montmorillonite

$(Na,Ca)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O$

- **anion conductive** — >1400 mS/cm at 110°C
- **mechanically strong** — Elastic modulus >8 MPa; elongation at break <20
- **durability** — promising (but not fully known)

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F.Ublekov, I. Radev, V. Sinigersky, M. Natova, H. Penchev, Mater. Lett. 219 (2018) 131-133

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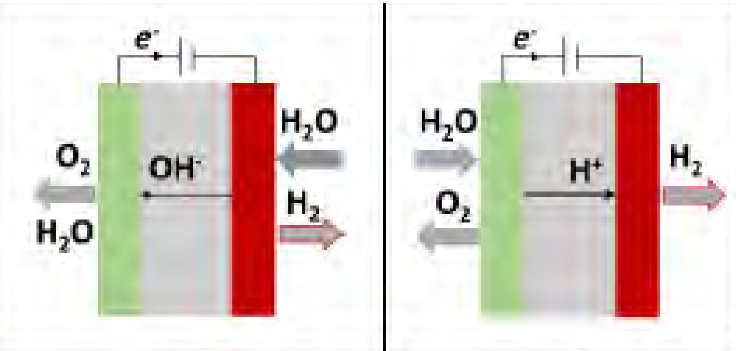
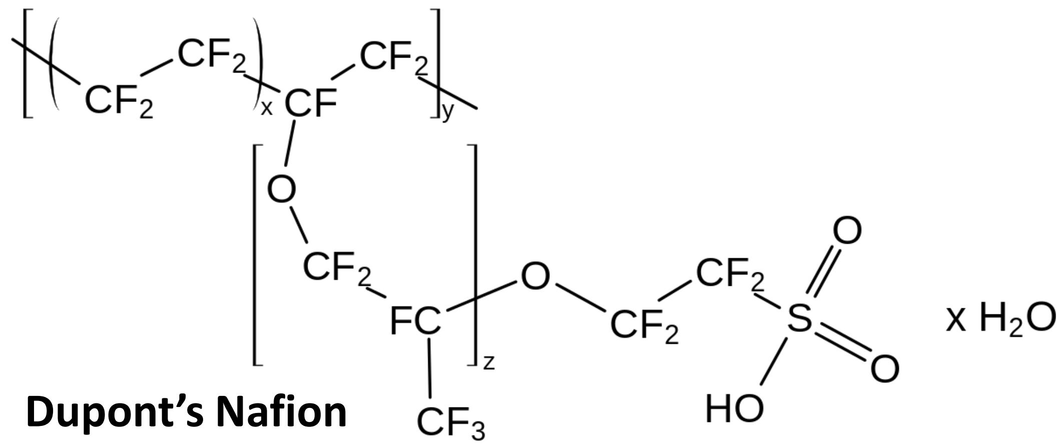
1869

Electrolysis with proton exchange membranes



AEM	PEM
OH^-	H^+
20-80°C	20-200°C
solid (polymeric)	solid (polymeric)
$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$	$2H_2O \rightarrow 4H^+ + O_2 + 4e^-$
Ni	IrO_2, RuO_2 $Ir_xRu_{1-x}O_2$ Supports: TiO_2, ITO, TiC
$4H_2O + 4e^- \rightarrow 4OH^- + 2H_2$	$4H^+ + 4e^- \rightarrow 2H_2$
$NiFe_2O_4$	Pt/C MoS_2

Proton Exchange Membrane (PEM):



Dupont's Nafion

Electrocatalysts:

Acidic nature of Nafion: limits catalysts to rare and expensive platinum-group metals

State-of-the-art MEA

(Membrane Electrode Assembly) :

IrRuOx / Nafion / Pt

PGM-free HER electrocatalysts for PEM electrolysers

Catalyst	Tafel slope (mV/dec)	Exchange current density (mA/cm^2)	Current density i (mA/cm^2)	Overpotential at current density i (mV)
Amorphous MoS_3 film	40	0.0013	2	170
MoS_2 nanoparticles on graphene	41	-	10	150
MoS_2 nanosheets	50	0.009	10	180
Pt-MoS_2 nanosheets on carbon fibers	53.6	-	10	35
CoS_2 nanowire	51.6	0.015	10	145
FeP on candle soot	58	0.22	10	112
FeP nanowire	38	0.42	10	55
CoP/CNTs	57	0.13	10	115
CoP nanowires	51	0.288	10	67
CoP nanoparticles	50	0.13	20	85
Ni_5P_4 nanocrystals	42	0.057	10	105
NiP_2 / C-nanospheres	**46**	**0.49**	**-**	**-**
Mo/P/S	50	0.2	-	-
WP_2 nanorods	52	0.013	10	148
C_3N_4 layers on nitrogen-doped graphene	49	0.43	10	80
Mo_2C-WC nanowire	56	0.0047	80	184
$Co_{0.6}Mo_{1.4}N_2$	-	0.000015	10	200
Mo_2N	100	-	10	381
Mo_2C	56	-	10	198

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F.M. Sapountzi, J.M. Gracia, C.J. Weststrate, H.O.A. Fredriksson, J.W. Niemantsverdriet, Prog. Energy Combust. Sci. 58 (2017) 1-35

PGM-free HER electrocatalysts for PEM electrolysers

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Mo/P/S	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	381
[illegible]	[illegible]	-	10	198

Transition metal phosphides show promise as HER electrocatalysts in acidic conditions

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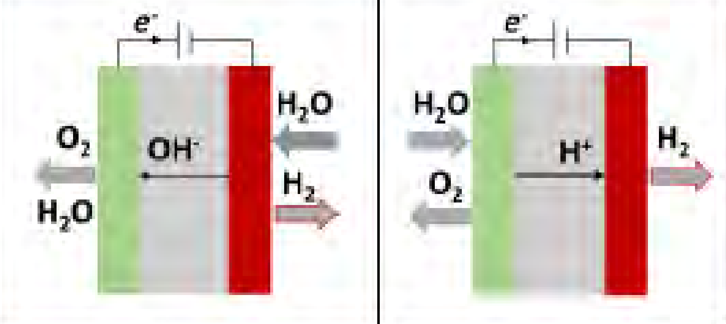
Exploring new HER/OER electrocatalysts: Fundamental studies

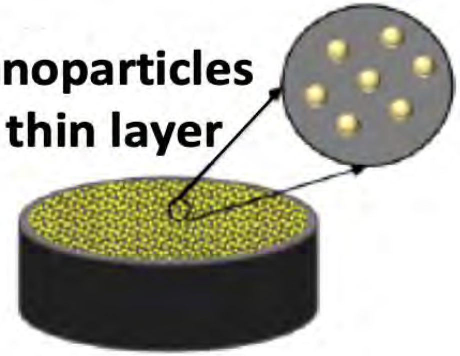


AEM	PEM
OH^-	H^+
20-80°C	20-200°C
solid (polymeric)	solid (polymeric)
$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$	$2H_2O \rightarrow 4H^+ + O_2 + 4e^-$
Ni	IrO_2, RuO_2 $Ir_xRu_{1-x}O_2$ Supports: TiO_2, ITO, TiC
$4H_2O + 4e^- \rightarrow 4OH^- + 2H_2$	$4H^+ + 4e^- \rightarrow 2H_2$
$NiFe_2O_4$	Pt/C MoS_2

2D electrocatalysts

- fundamental research
- well-defined area
- limited reaction zone

nanoparticles or thin layer



- Model-type electrodes with low surface area
- Testing under simulated conditions (immersed in acidic or alkaline solutions)

99% of literature on novel materials for H_2O electrolysis follows this methodology

>1500 published articles:
promising materials have been identified
i.e. FeP, MoS_2, $LaNiO_3$

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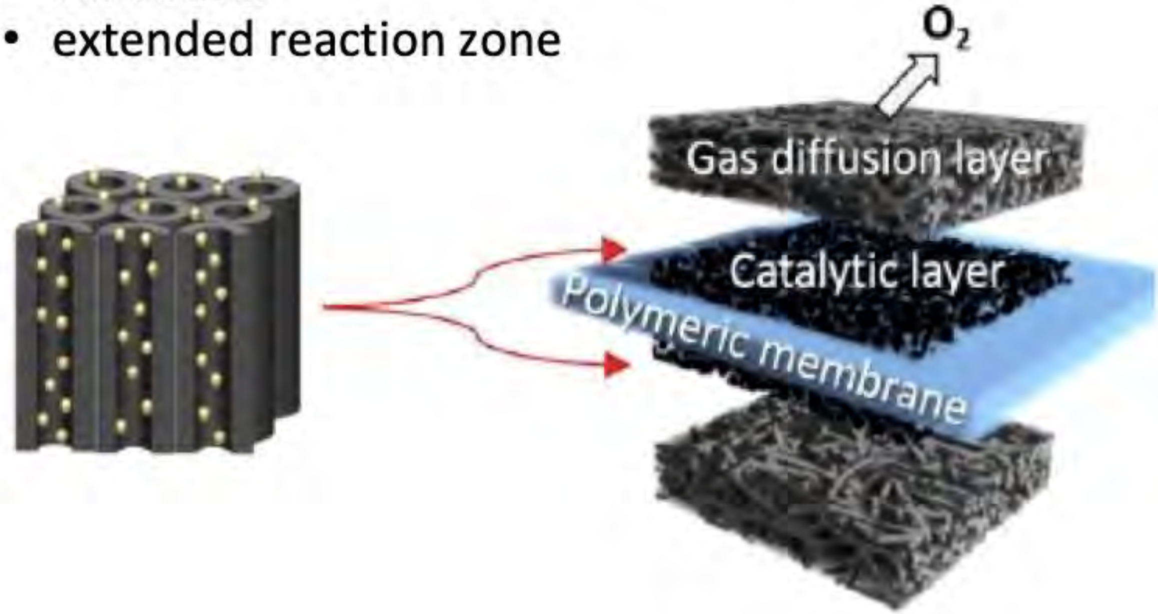
Implementing new electrocatalysts in real electrolysers

3D Electro catalysts

- applied studies
- dispersed nanoparticles on high-surface area substrates
- extended reaction zone

Membrane-electrode assembly (MEA)

solid electrolyte between two electrode layers



single cell

stack

Only 1% of literature studies on H_2O electrolysis report alternative electrocatalysts in zero-gap electrolysers…

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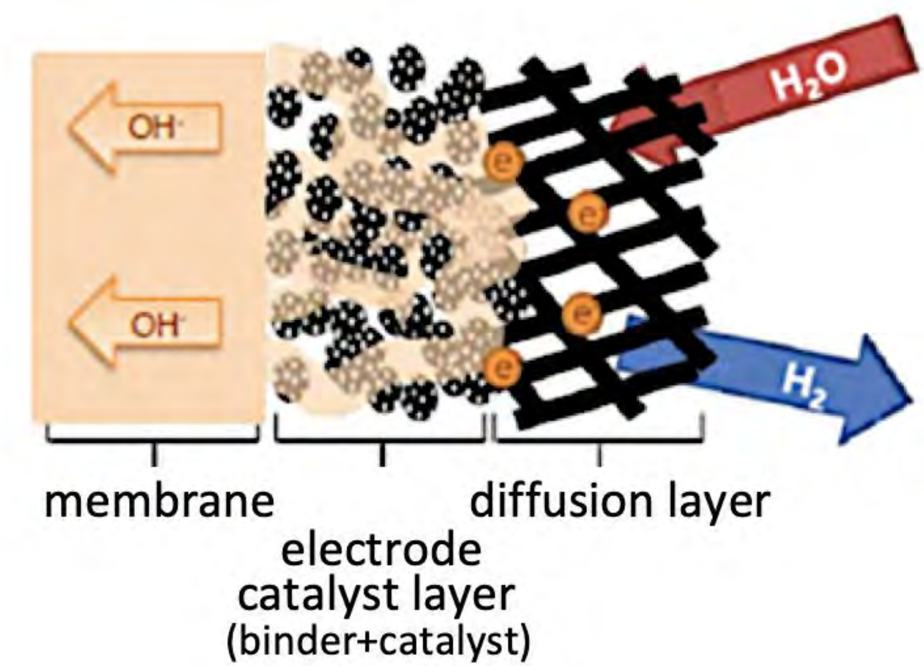
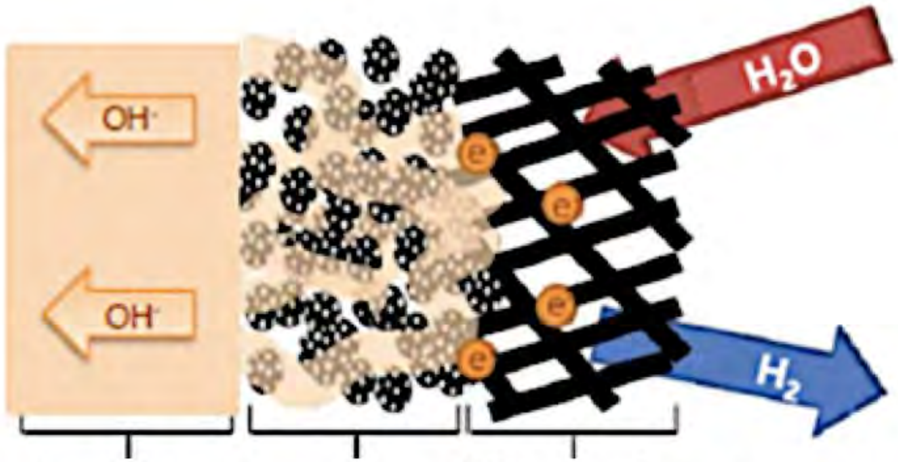
X. Sun, K. Xu, C. Fleischer, X. Liu, M. Grandcolas, R. Strandbakke, T.S. Bjorheim, T. Norby, A. Chatzitakis, Catalysts 8 (2018) 657

Implementing new electrocatalysts in real electrolysers



Picture from:
C.M. Kyung, L.Ahyoun, L.S. Young, K. Hyoung-Juhn, Y.S. Jong, S. Yung-Eun, P. Hyun, J.J. Hyun, J. Electrochem. Sci. Technol. 8 (2017) 183-196

Implementing new electrocatalysts in real electrolysers



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At Syngaschem we focus on the design of Membrane-Electrode Assemblies: understand and improve the polymer/electrode interface

Diffusion layer (porous, e^- conductor)

- Kind: C, Ti, Ni-based
- Hydrophobicity: PTFE loading

Electrocatalyst

- Nature-composition
- Catalyst loading
- Structural characteristics

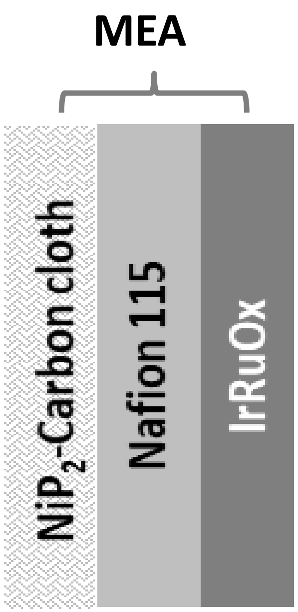
Binder (ionomer)

- chemical composition
- loading

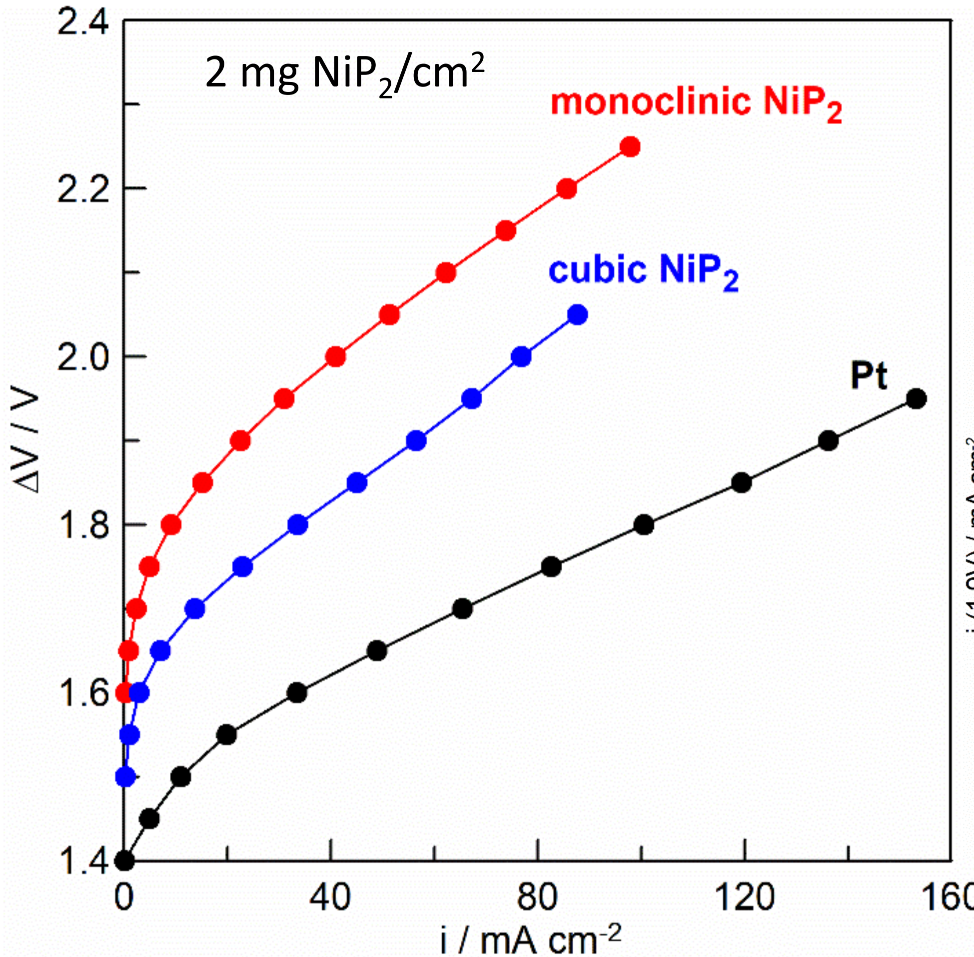
Method of electrode preparation:

- electrodeposition, ALD, spraying, sputtering, printing

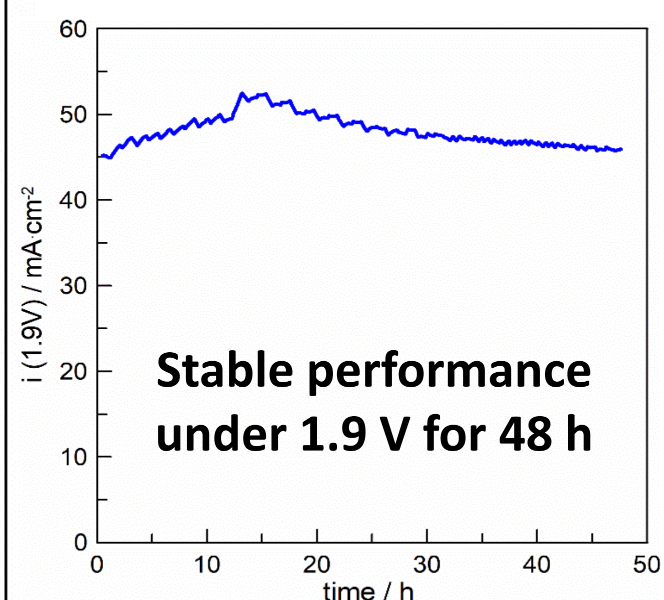
Example: Transition metal phoshides
alternative for Pt in Hydrogen Evolution



PEM water **vapor** electrolysis at 25°C



NiP_2



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Iowa State University

INL International Iberian Nanotechnology Laboratory

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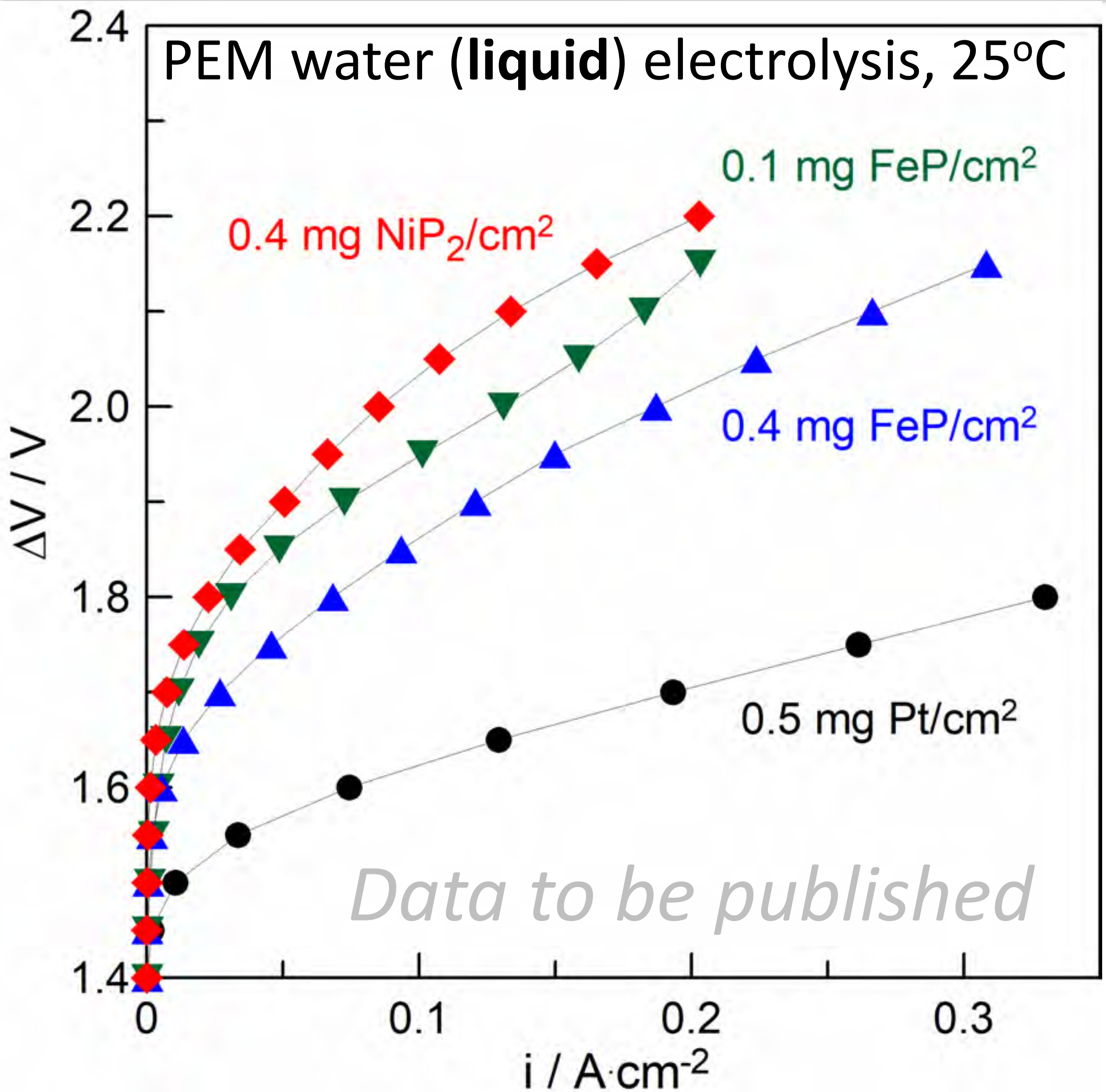
B. Owens-Baird, J. Xu, D. Petrovykh, O. Bondarchuk, Y. Ziouani, N. Gonzalez, P. Yox, F. Sapountzi, J.W. Niemantsverdriet, Y. Kolen'ko, K. Kovnir, Chem. Mater. 31 (2019) 3407-3418

Example: Transition metal phoshides
alternative for Pt in Hydrogen Evolution



FeP

NiP_2 : unsupported

FeP : supported on porous conductive carbon

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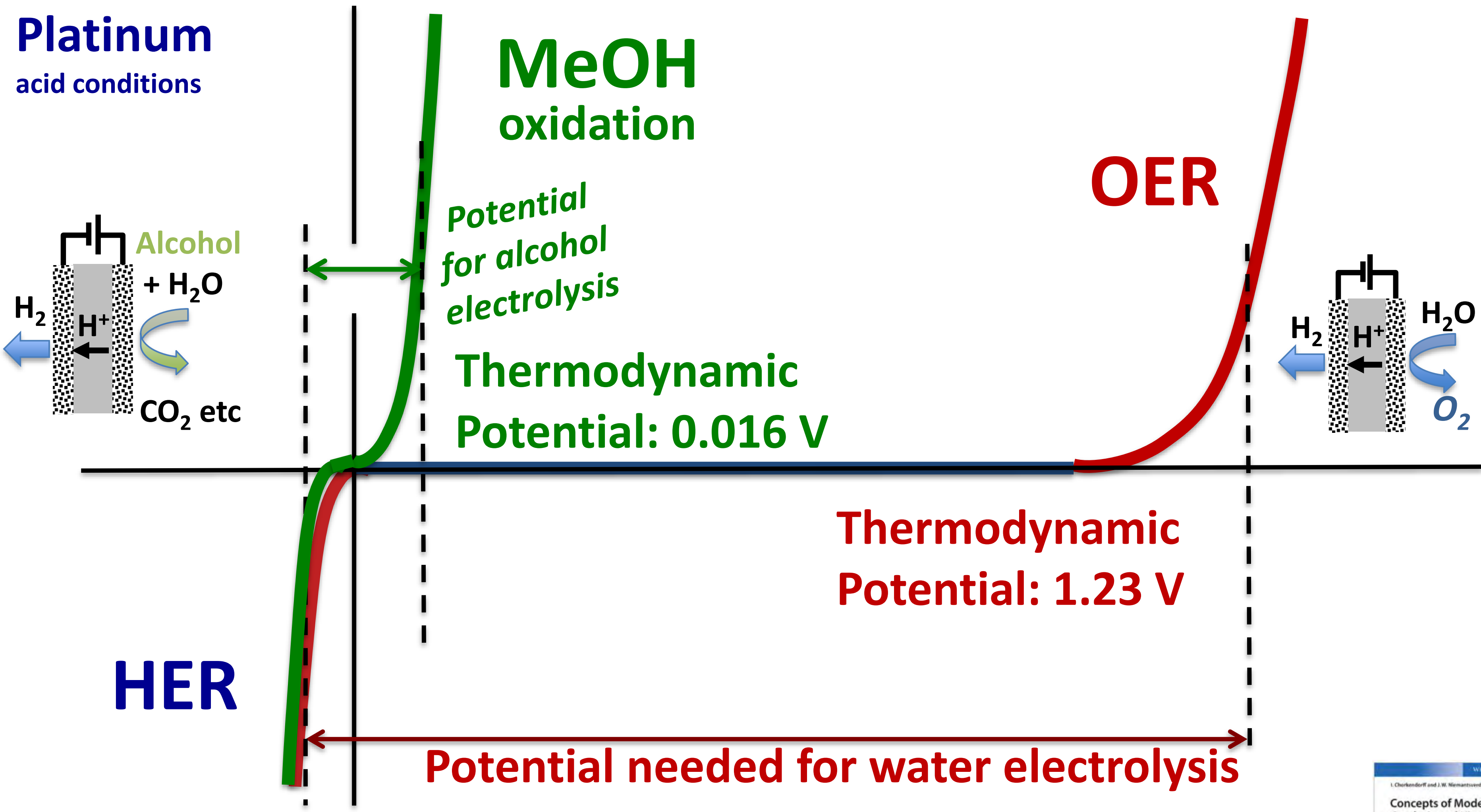
INL
INTERNATIONAL IBERIAN NANOTECHNOLOGY LABORATORY

Collaboration with
Y. Kolenko and K. Kovnir

IOWA STATE UNIVERSITY

Electrolysis of Alcohol vs Water



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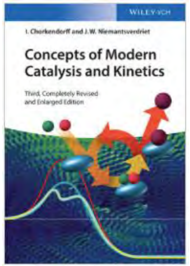
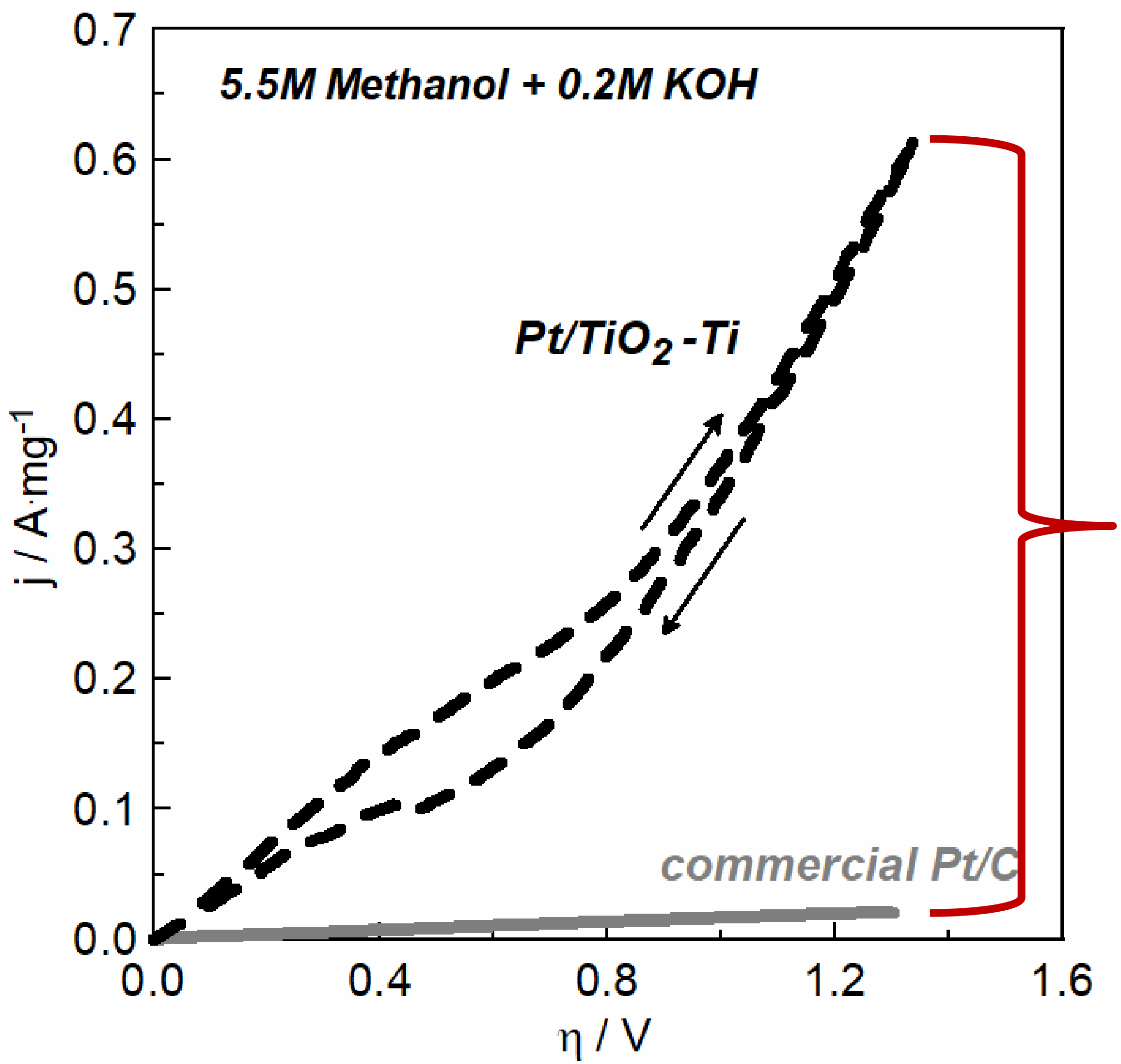
Ib Chorkendorff, Hans Niemantsverdriet, Concepts of Modern Catalysis and Kinetics, 3rd Edition, Wiley-VCH, 2017



Our success story in using Pt effectively



DIFFER Dutch Institute for Fundamental Energy Research

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TU/e

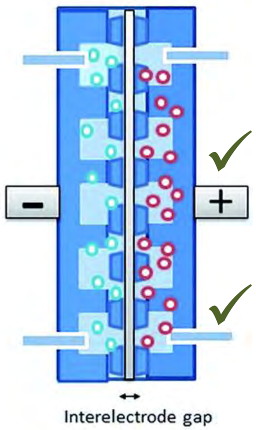
30-fold enhancement

by optimized Pt – diffusion layer geometry

F.M. Sapountzi, V. Di Palma, G. Zafeiropoulos, H. Penchev, M. Verheijen, M. Creatore, F. Ublekov, V. Sinigersky, W. Arnold Bik, H.O.A. Fredriksson, M.N. Tsampas, J.W. Niemantsverdriet, Int. J. Hydrogen Energy 44 (2019) 10163

Conclusions

Zero-gap electrolysis



✓ efficient

✓ responsive

AEM		PEM
OH^- conductive	Counter ion	H^+ conductive
Compatible with Ni-based electrocatalysts	Features	High ion conductivity Excellent membrane stability
Lower ion conductivity Lower membrane stability	Issues	High cost of electrocatalysts

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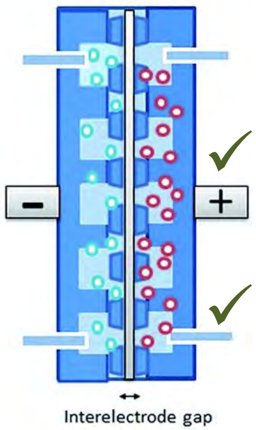
Conclusions

Zero-gap electrolysis



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Conclusions

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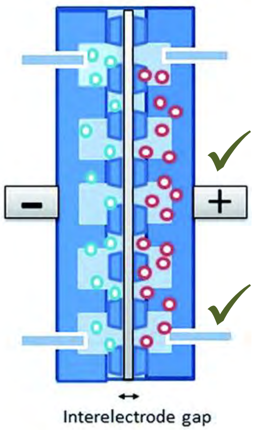

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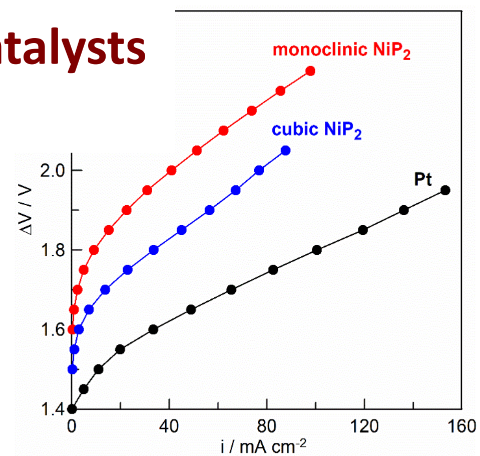
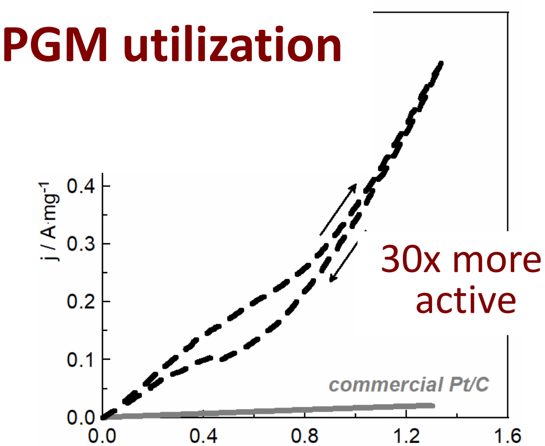
Novel PGM-free catalysts

phosphides



Improved PGM utilization

by ALD



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