Accelerated Stress Test (AST) Development

Advanced Liquid Alkaline Water Electrolysis Experts Meeting
Jan 25th 2022

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LA-UR-22-20922

OUTLINE

- Alkaline Water Electrolyzers
  - Comparison of PEMEC and AWE systems
  - Components and degradation mechanisms in AWE
- AST development
  - Electrolzyer AST development (AWE focus)
  - PEMEC AST development
  - AWE AST development
- Acknowledgements
- Conclusions

AWE

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PEMEC vs AWE vs AEMEW systems

Table 1. State-of-the-art low temperature water electrolysis technologies

ELECTROLYSIS TYPE	PEMWE Proton Exchange Membrane	AWE Alkaline	AEMWE Anion Exchange Membrane
Charge carrier (1)	H^+	OH^-	OH^-
Reactant	Liquid Water	Liquid Water	Liquid Water
Electrolyte	Proton exchange membrane	NaOH or KOH 20-40 wt.% / water	Anion exchange membrane
Anode Electrode	IrO_2 IrO_2/Ti_4O_7 $Ir_xRu_yTa_zO_2$, Ir black	Co_3O_4, Fe, Co, Mn Mo, P, S, $NiFe(OH)_2$, Fe(Ni)OOH, oxides, hydroxides, borides, nitrides, carbide-based catalysts	IrO_x $Pb_2Ru_2O_{6.5}$, $Bi_{2.4}Ru_{1.6}O_7$, NiO_x, Ni-Fe, $Li_xCo_{3-x}O_4$, $Cu_{0.6}Mn_{0.3}Co_{0.21}O_4$, $CuCoO_x$
Cathode electrode	Pt/C	Raney®-Ni, Co, Cu, NiCu, NiCuCo, Ni-Co-W, Ni-Cu-Zn-B, Ni-Co, Ni-Fe, Ni-Co-Mo, NiCoZn, Raney®-Co, Ni-Mo, Ni-S, Ni-rare earth alloys	Raney®-Ni, NiO, Co based catalyst $Ni/(CeO_2\text{-}La_2O_3)/C$ Pt/C
Current density	0.2-8.0 A/cm²	0.2-2.5 A/cm²	0.2-0.8 A/cm²
OperatingTemperature	20-80 °C (2)	40-90 °C	40-60 °C
Pressure H_2 out (3)	$(10-30)\cdot 10^5$ Pa	$(10-30)\cdot 10^5$ Pa	$(10-30)\cdot 10^5$ Pa
Cathode reaction (H_2 evolution reaction HER) (4)	$4H^+(aq) + 4e^- \rightarrow 2H_2(g)$	$4H_2O(l) + 4e^- \rightarrow 2H_2(g) + OH^-(l)$	$4H_2O(l) + 4e^- \rightarrow H_2(g) + 4OH^-(aq)$
Anode reaction (O_2 evolution reaction OER)	$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$	$4\,OH^-(aq) \rightarrow 2H_2O(l) + O_2(g) + 4e^-$	$4\,OH^-(aq) \rightarrow 2\,H_2O(l) + O_2(g) + 4e^-$

Source: JRC, 2020

AWE

- Established commercial technology
- Low cost separator and electrode materials
- Excellent long term durability of base system

- Highly corrosive supporting electrolyte
- Complex balance of plant
- Lower current density operation
- High crossover
- Several Advances are recent and not established:
  - Membrane separators
  - Zero gap designs
  - Advanced electrodes

EU harmonised protocols for testing of low temperature water electrolysers
G. Tsotridis, A. Pilenga. 2021

https://publications.jrc.ec.europa.eu/repository/handle/JRC122565
-20922

AWE systems

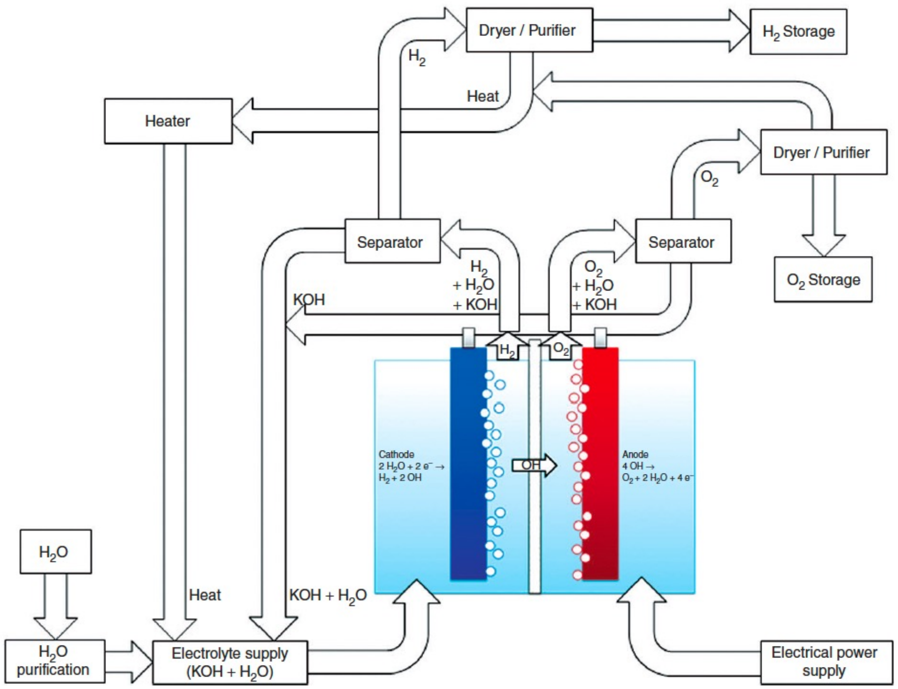

FIGURE 6 | Illustration of an alkaline water electrolyzer system.

- Complex BOP compared to PEM
- Pump and mix caustic from anode and cathode
- Have to separate the gases
- Conventional system cannot operate at low current densities due to high crossover

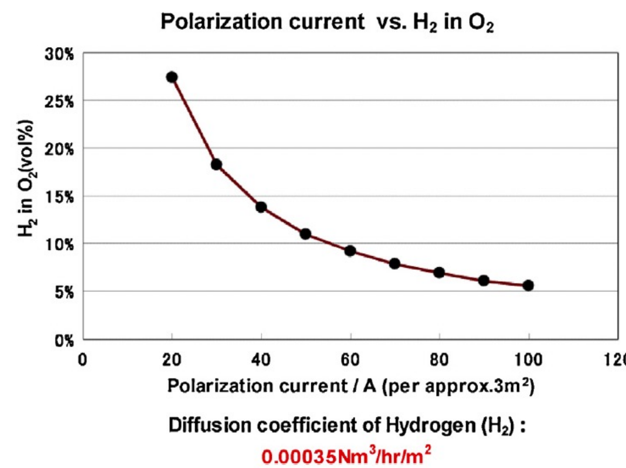

Fig. 14. Hydrogen crossover into anodic chamber under protection conditions.

WIREs Energy Environ 2015, 4:365–381. doi: 10.1002/wene.150

A. Manabe et al. / Electrochimica Acta 100 (2013) 249– 256

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AWE Cell designs

- Gap (conventional) and zero gap (recent) cell designs
- Zero gap cells can operate at higher current densities
- Zero gap cells are not as durable

<u>Single cell designs available in the literature</u>

- Polyether ether ketone (PEEK) is used for the cell structure
- Nickel plates (BGH, 99.5%) electrodes
- Zirfon diaphragms (Agfa, Perl utp 500) separators
- Pumps to circulate electrolyte, heaters to heat electrolyte and DC power supply,

Lab-Scale Alkaline Water Electrolyzer for Bridging Material Fundamentals with Realistic Operation

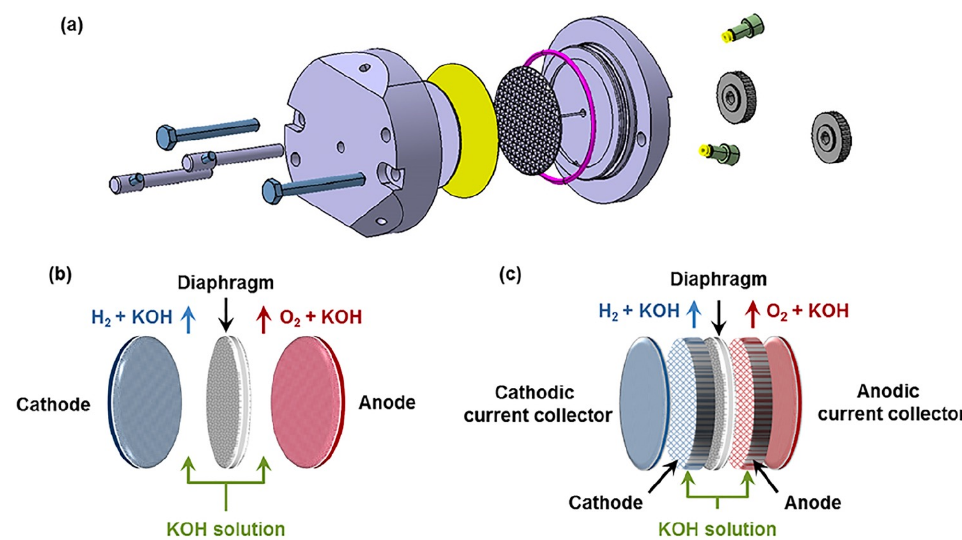

Figure 2. Schematic structures of electrolysis cell (a), gap electrode assembly (b), and zero-gap electrode assembly (c).

DOI: 10.1021/acssuschemeng.7b04173

ACS Sustainable Chem. Eng. 2018, 6, 4829–4837

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AWE Components

Table 6
Oxygen overpotential of different electrode materials [taken from [104]]

Composition formula	Method	T (°C)	Electrolyte	C(mol dm^{-3})	j (Am^{-2})	η_{oxygen} (mV)	Ref.
Ni + Spinel type Co_3O_4	Thermo-decomposition	25	KOH	1	1000	235 ± 7	[105]
Ni + La doped Co_3O_4	Thermo-decomposition	25	KOH	1	1000	224 ± 8	[105]
MnOx modified Au	Electro-deposition	25	KOH	0.5	100	300	[106]
Li10% doped Co_3O_4	Spray pyrolysis	RT	KOH	1	10	550	[107]
Ni	N/A	90	KOH	50 wt%	1000	300	[108]
$La_{0.5}Sr_{0.5}CoO_3$	Spray-stiner	90	KOH	50 wt%	1000	250	[108]
$Ni_{0.2}Co_{0.8}LaO_3$	Plasma jet projection	90	KOH	50 wt%	1000	270	[108]

399

Table 7
Hydrogen overpotential of different electrode materials [taken from [104]]

Composition formula	Method	T (°C)	Electrolyte	C(mol dm^{-3})	j (Am^{-2})	$\eta_{hydrogen}$ (mV)	Ref.
Ni-Fe-Mo-Zn	Co-deposition	80	KOH	6	1350	83	[109]
Ni-S-Co	Electro-deposition	80	NaOH	28 wt%	1500	70	[110]
Ni50%-Zn	Electro-deposition	N/A	NaOH	6.25	1000	168	[111]
$MnNi_{3.6}Co_{0.75}Mn_{0.4}Al_{0.27}$	Arc melting	70	KOH	30 wt%	1000	39	[112]
Ti_2Ni	Arc melting	70	KOH	30 wt%	1000	16	[113]
Ni50%Al	Melting	25	NaOH	1	1000	114	[114]
Ni75%Mo25%	Co-deposition	80	KOH	6	3000	185	[115]
Ni80%Fe18%	Co-deposition	80	KOH	6	3000	270	[115]
Ni73%W25%	Co-deposition	80	KOH	6	3000	280	[115]
Ni60%Zn40%	Co-deposition	80	KOH	6	3000	225	[115]
Ni90%Cr10%	Co-deposition	80	KOH	6	3000	445	[115]

- Separators:
  - Asbestos
  - Polysulfone matrix and ZrO_2 (Zirfon)
  - Polyphenylene sulfide (Ryton)

- Electrodes

  Anode
  - High surface area Ni
  - Raney® Ni
  - Spinels
  - Perovskites

  Cathode
  - High surface area Ni
  - Stainless steel

Journal of Energy Storage 23 (2019) 392–403

Anode/Cathode durability (elevated temperature)

Table II. Overview on stability of catalysts tested in high-temperature alkaline electrolysis. T: temperature, t: test duration.

	Material	T	KOH	conditions	t	degradation
Anode	RuO_2[45]	>100 °C	50 wt.%	0.1–1 A cm^{-2}	few h	dissolves
	Raney Ni [84]	100 °C	40 wt.%	0–0.4 A cm^{-2}	7200 h	slow
	[85]	160 °C	—	—	—	unstable
	[86]	200 °C	35 wt.%	1 A cm^{-2}	100 h	unstable
	porous Co[87]	90 °C–130 °C	30–40 wt.%	—	—	fast
	porous $NiCo_2$[87]	90 °C–130 °C	30–40 wt.%	1 A cm^{-2}, $\eta < 270$ mV	3000 h	stable
	Co_3O_4/Ni[88]	120 °C	40 wt.% NaOH	1 A cm^{-2}	10,000 h	slow
	Co-oxide[31]	200 °C	45 wt.%	1.5 V	24 h	stable
	[31]	250 °C	45 wt.%	1.5 V	100 h	unstable
	La–Ni(−Fe)-perovskites[89]	100 °C	31, 45 wt.%	ex situ	168 h	stable
	[89]	220 °C	31, 45 wt.%	ex situ	168 h	unstable
	Co–(Ni–Fe) ox. synth. in situ[87,90]	90 °C–130 °C	30–40 wt.%	1 A cm^{-2}	> 400 h	unstable
	$La_{0.5}Sr_{0.5}CoO_3$/porous Ni[44]	160 °C	40 wt.%	1 A cm^{-2}	2800 h	stable
	Ag-nanowires/NiFeCrAl foam[2]	200 °C	45 wt.%	0.5 A cm^{-2}	400 h	stable
	Ni–Fe–Hydroxides				not tested at HT	
Cathode	Raney Ni[85]	190 °C	40 wt.%	ex situ		unstable
	[46]	200 °C	NaOH	intermittent pol.		unstable
	[86]	200 °C	35 wt.%	1 A cm^{-2}	100 h	stable
	Ni-sulfide[6,46,91]	<110 °C	—	—	—	unstable
	Ti-/Mo-doped porous Ni[44,85]	160 °C	40 wt.%	1 A cm^{-2}	8000 h	stable
	Raney NiCo[6]	—	—	—	—	stable
	inconel foam[2]	200 °C	45 wt.%	0.5 A cm^{-2}	400 h	stable
	Ru-film/Ni[90]	120 °C	40 wt.%	1 A cm^{-2}	600 h	stable

Journal of The Electrochemical Society, 2021 168 114501

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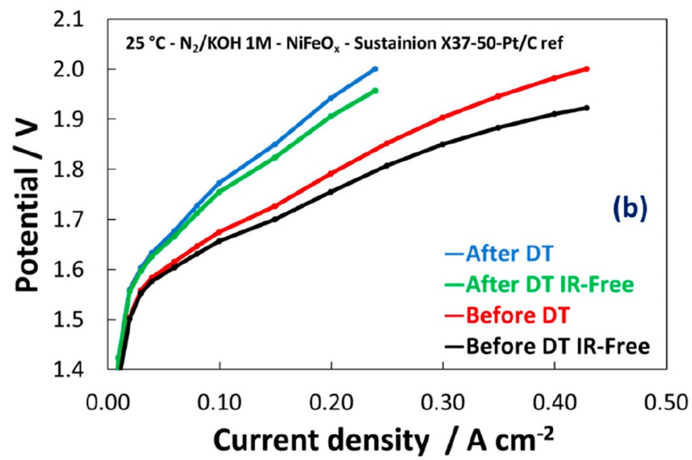
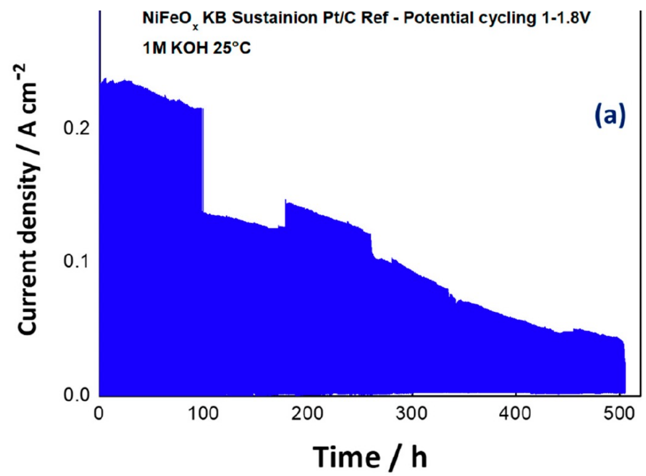
Anode durability

- Ni electrode dissolution rate is low
- Mainly loss in porosity by accumulation of oxidation products in the microstructure

- Advanced electrodes have stability issues. E,g, NiFeOx shown in the right
- Numerous other electrodes have also shown increased overpotential with operating hours





Energies 2020, 13, 1720

Electrolysis was carried out at 1000 mA/cm 2, in 35% KOH at 200~ under 30 atm pressure. During 250h of electrolysis, anode porosity decreased from about 45% to about 20% as corrosion products accumulated within the anode.

Alkaline Water Electrolysis Anode Materials
D. E. Hall. JECS. Feb 1985

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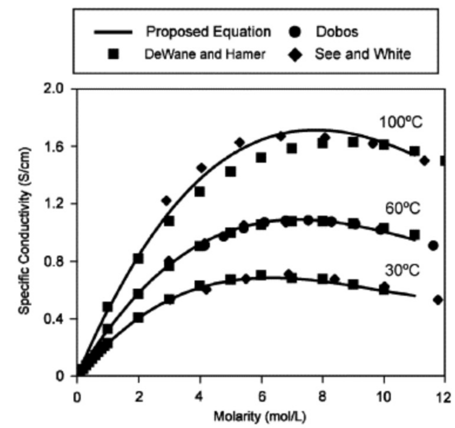
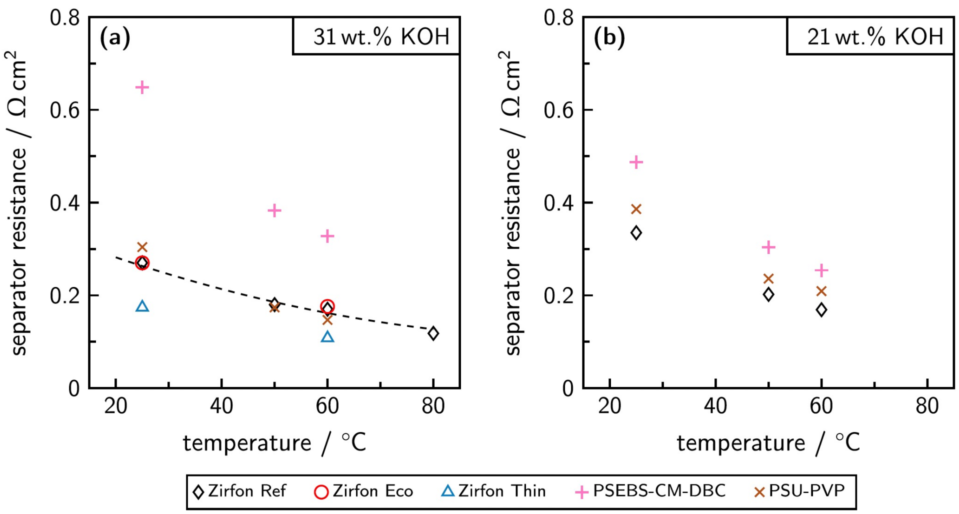
Separator durability

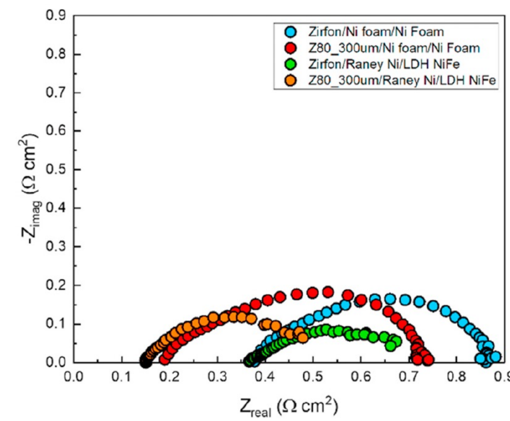
- Commercial porous separators with proven stability in high concentration NaOH and KOH
- Membrane separators are newer (unproven long term stability)
- Higher temperature operation can enhance supporting electrolyte conductivity and electrolyzer performance
- Track Bubble point, ASR, H_2 permeability



[International Journal of Hydrogen Energy](#)
[Volume 32, Issue 3](#), March 2007, Pages 359-36



Journal of The Electrochemical Society, 2021 168 014510



Journal of Membrane Science 616 (2020) 118541

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AST Development

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Durability (Stressors)

Table 20. Agreed settings of AWE stressorsfor AWE single cell and short stack testing

	PARAMETERS	UNIT	REFERENCE Setting	Cell Temperature Stressor settings		H2 Pressure Stressor settings	Electrolyte Inlet Flowrate Stressor settings	
				Test 1	Test 2	Test 3	Test 4	Test 5
	Cell/stack temperature	°C	80	50	100	80	80	80
ANODE	Electrolyte inlet temperature	°C	80	50	100	80	80	80
ANODE	Minimum Electrolyte inlet flowrate	$mL.cm^{-2}.min^{-1}$	1	1	1	1	0.25	2
CATHODE	Electrolyte inlet temperature	°C	80	50	100	80	80	80
CATHODE	Minimum Electrolyte inlet flowrate	$mL.cm^{-2}.min^{-1}$	1	1	1	1	0.25	2
CATHODE	Hydrogen outlet pressure	kPa	500	500	500	3,000(10)	500	500

Source: JRC, 2020

EU harmonised protocols for testing of low temperature water electrolysers

G. Tsotridis, A. Pilenga. 2021

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Durability (Stressors)

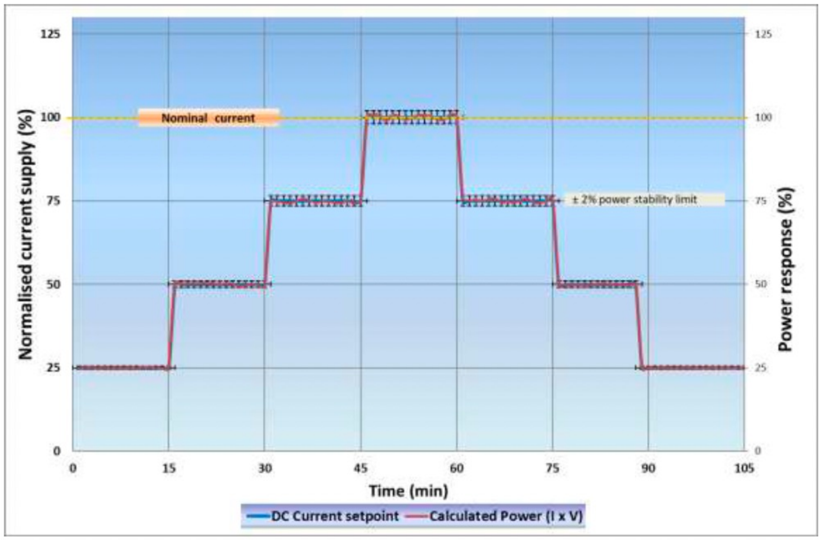
- JRC has defined load profiles to evaluate the durability of electrolyzers

Table 26. Agreed AST load profile

STEPS	AST load profiles
1	Flexibility
2	Reactivity

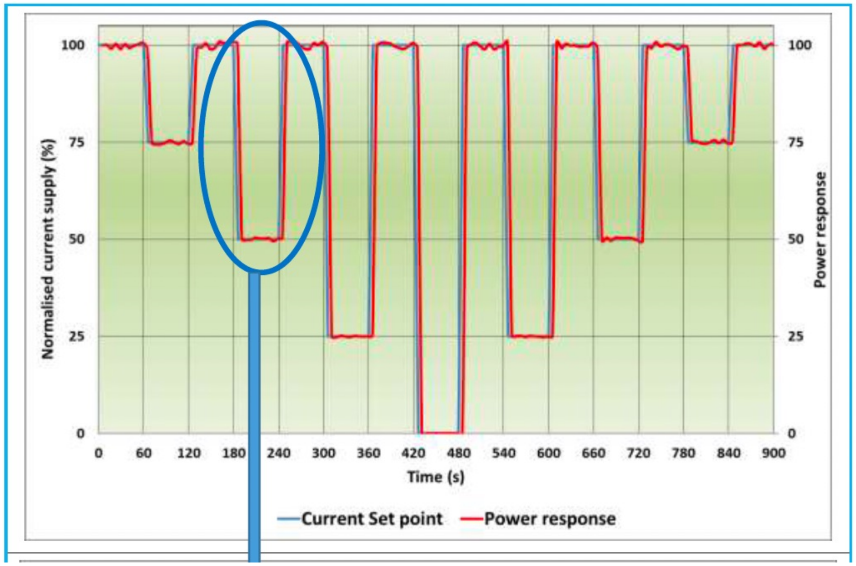
Source: JRC, 2020

Figure 25. 100 % of nominal current flexibility profile



Source: JRC, 2020

Figure 27. Reactivity profile



EU harmonised protocols for testing of low temperature water electrolysers. G. Tsotridis, A. Pilenga. 2021

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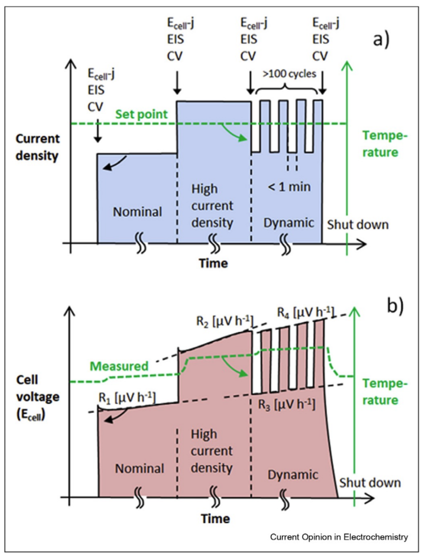
Drive cycles and degradation

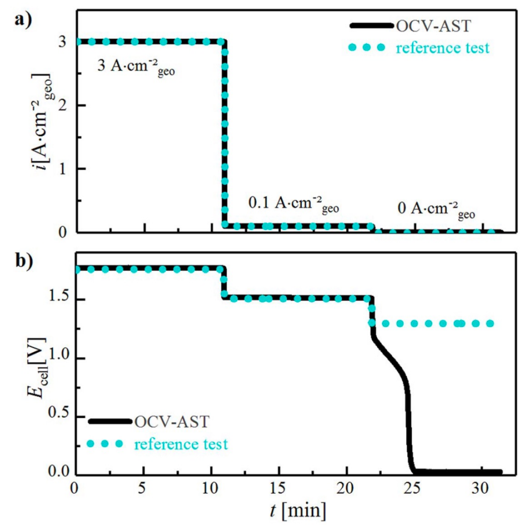
Next generation electrolyzer:

Follow load and not just full-power/idle mode

Meet cost and performance targets with lower catalyst loadings, thinner membranes, thinner PTL coatings etc.



P. Aβman et al., Current Opinion in Electrochemistry 2020, 21:225–233



A. Weiβ *et al., Journal of The Electrochemical Society*, **166** (8), 2019 F487-F497

- Need to develop catalyst specific ASTs that are relevant to load following applications
- Need to capture : Dynamic operation, high current operation, and shutdown

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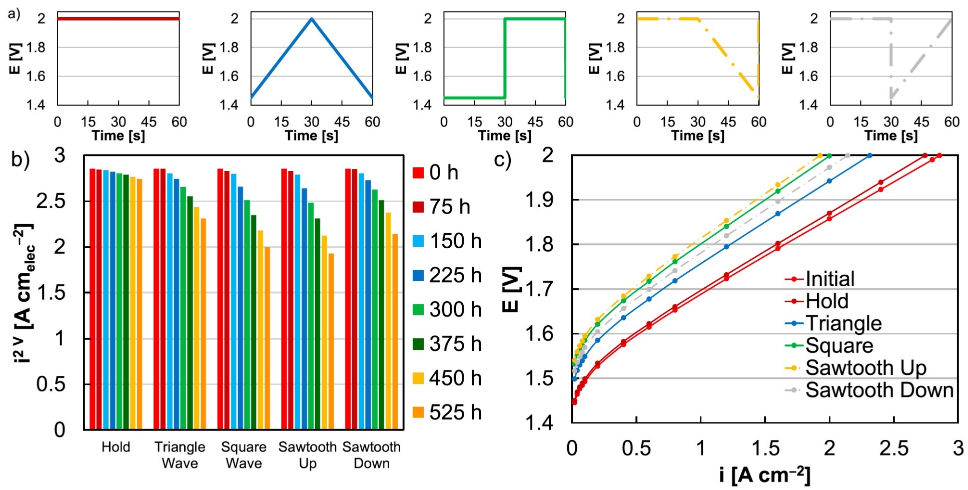
PEMEC Catalyst ASTs



Journal of The Electrochemical Society, 166 (15) F1164-F1172 (2019)

Systematic study of the effect of catalyst loading, and dynamic operation on electrolyzer durability

- Lower loadings and dynamic operation significantly accelerate degradation

Developed fundamental understanding of degradation mechanisms leading to ASTs (electrocatalyst)

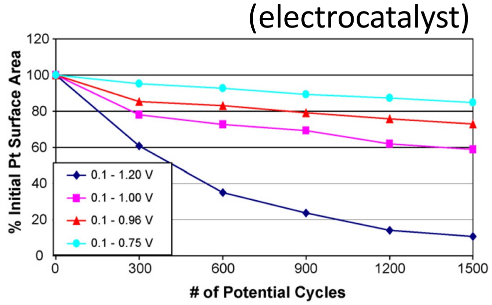
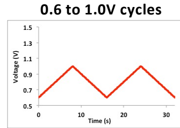


Fig. 2. Potential effect on catalyst surface area loss.

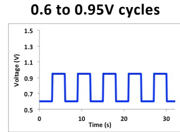
R.L. Borup et al., Journal of Power Sources 163 (2006) 76-81

0.6 to 1.0V cycles



Target = 50 hours

0.6 to 0.95V cycles



Target = 40 hours

- NREL has identified how various potential waveforms affect degradation at different catalyst loadings
- Better understand degradation mechanisms and perform parametric study
- Develop catalyst specific AST to rapidly evaluate state of the art unsupported IrOx anode catalyst and correlate to degradation observed in electrolyzer duty cycle

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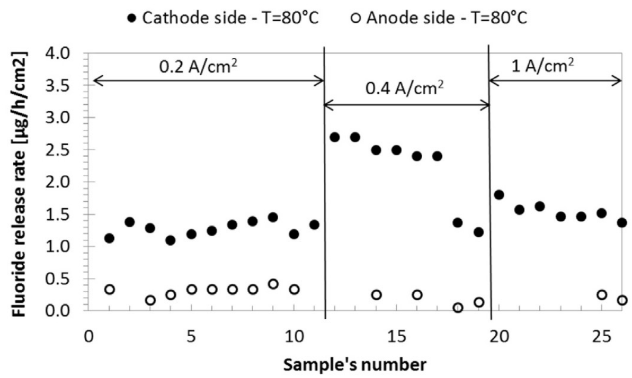
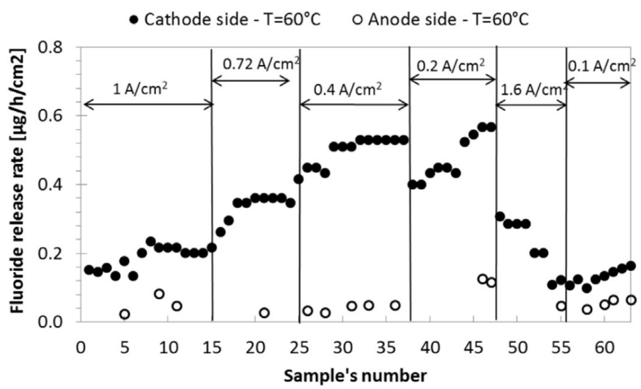
PEMEC Membrane ASTs

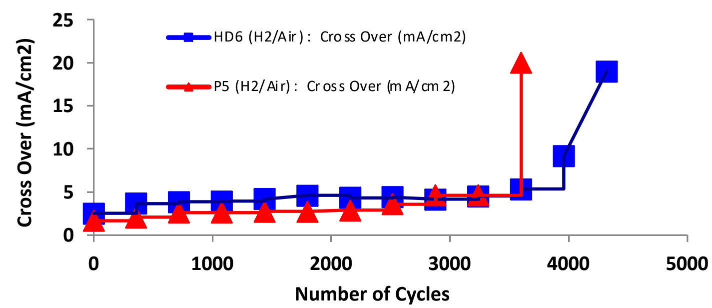
Cathode side membrane degradation observed, accelerated by Temp and low currents

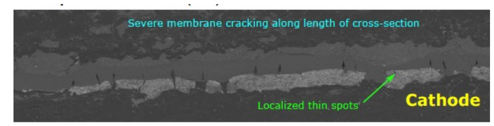




M. Chandesris, Int. J. Hydrogen Energy, 40, 1353-1366 (2015)

Previously developed combined chemical/mechanical ASTs based on correlation to field data (membrane) developed for fuel cells





R. Mukundan et al., J. Electrochem. Soc., **165 (6)**, F3085-F3093 (2018)

- Evaluate influence of temp, current, partial pressure differential, shut-down/start up, and presence of Fe on membrane degradation
- Evaluate both fluoride emission rate and mechanical property changes during drive cycle experiments
- Develop membrane specific AST

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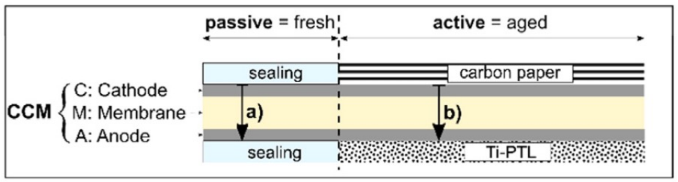
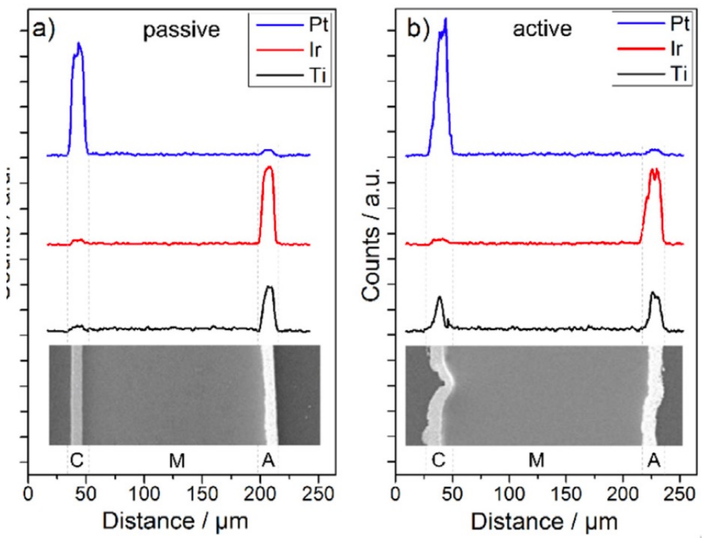
PEMEC PTL ASTs

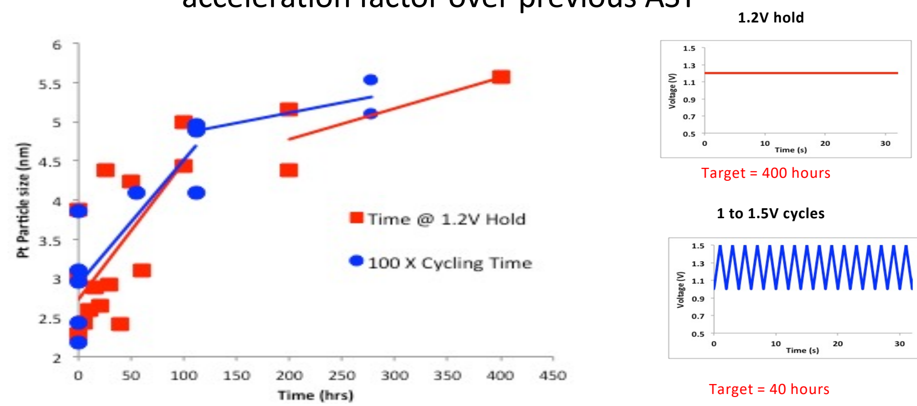
Ti leaching from un-coated PTLs is a significant source of degradation: Contact resistance increase and poisoning of anode catalyst





C. Rakousky et al, J. Power Sources. 326, 120-128(2016)

Have developed catalyst support AST with 100X acceleration factor over previous AST



N. Macauley et al., J. Electrochem. Soc., **165 (6)**, F3148-F3160 (2018)

- Evaluate corrosion rates (leaching rates and oxidation rates) of coated and un coated PTLs under different conditions
  - Temperature
  - Potential/current density
  - Track contact resistance and water transport
- Develop PTL specific AST

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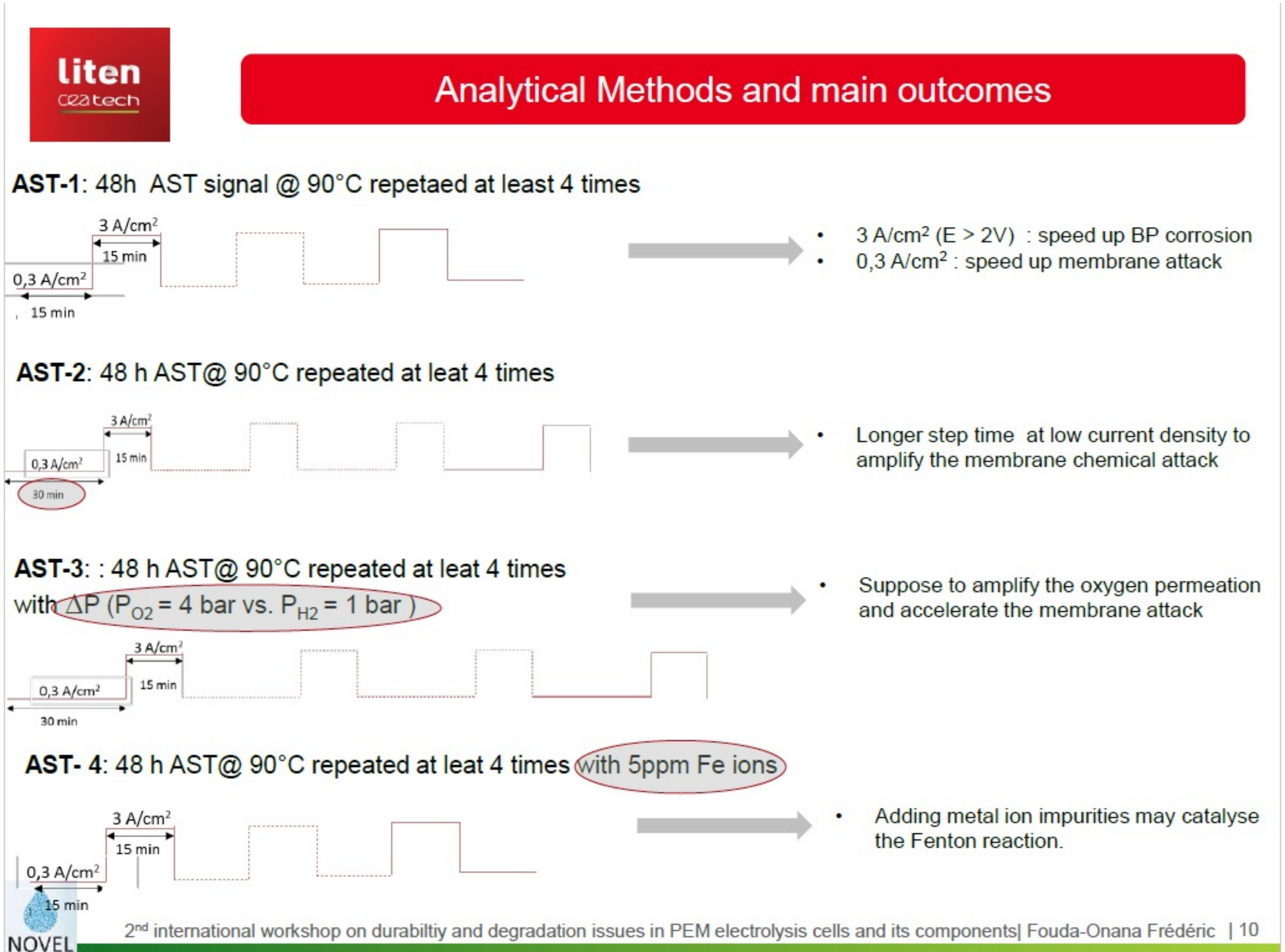
PEMEC AST development (Literature)



Dynamic operation results in 40X faster degradation rate than steady state hold

AST -2 demonstrates high degradation rates

AST -4 Need to evaluate with ppb levels of Iron (μgm/cm^2) in membrane can result in accelerated degradation

AWE ASTs

- High temperature evaluation of stability in supporting electrolyte (100 - 200 ^{o}C; 5- 10 M KOH)
- Dynamic operation
- Start-up and Shut-down
- High current density operation with low electrolyte flow (bubble formation)

- Catalysts: Ex situ aqueous measurements (mainly dissolution and not for morphology changes). Track CVs and RDE OER activity.

- Separators/Membranes : Ex situ aqueous chemical/mechanical stability. Especially for membranes and thinner separators. Track EIS, ASR, bubble point, porosity

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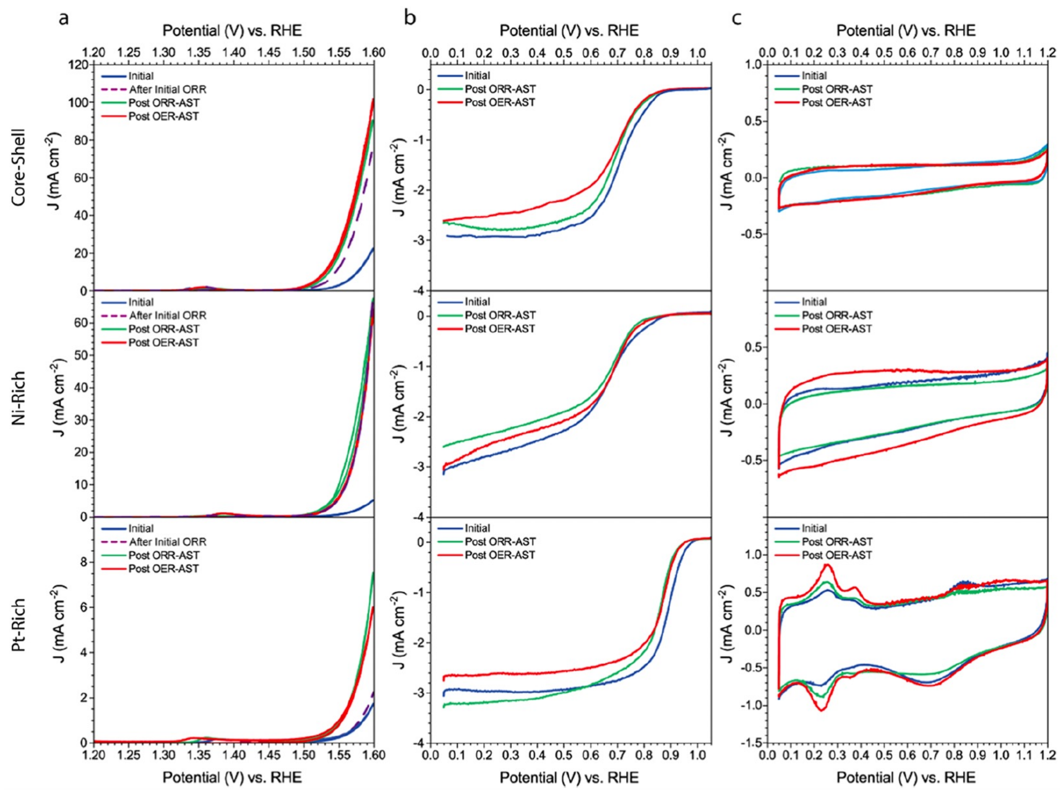
AWE Catalyst ASTs



- RDE setup with glassy carbon electrode
- Catalyst ink at 2 mg/ml inks
- 10 $\mu g/cm^2$ catalyst on disc
- 1 M KOH at 298 K
- Potential cycling at both ORR and OER conditions
- Evaluate stability with CVs and OER/ORR measurements

https://dx.doi.org/10.1021/acsaem.0c01356
ACS Appl. Energy Mater. 2020, 3, 8858–8870

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  - ORNL (Dave Cullen, Haoran Yu)
  - ANL (Debbie Myers)

- DOE - EERE – HFTO
  - Dave Peterson, Ned Stetson, Sunita Satyapal

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Conclusions

- Conventional materials used in AWE are very durable and there are no prescribed ASTs. > 10 years durability demonstrated in the field for various materials
- New materials and designs are unproven
  - Zerogap design
  - High temperature operation
  - Thinner separators
  - Membrane separators
- Electrolyzer ASTs with different duty cycles have been proposed for PEMEC, AWE and AEMWE
- Component specific ASTs need to be developed and validated
  - Electrodes need to be evaluated in-operando to track morphology changes
  - Electrodes can be evaluated in RDE environment to track chemical stability
  - Separators need to be evaluated in-operando to capture
  - Temperature probably the best accelerating factor

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