REVERSIBLE ZINC STORAGE FOR HYDROGEN PRODUCTION

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IZABW

Third International Zinc-air and other Zinc Batteries Workshop (3rd IZABW)

18th/19th of September 2023, Ulm Germany

AGENDA

- Project Partners
- Introduction of the Zn-H2 storage principle
- Full cell testing – catalyst stability
- Zinc deposition - charging
- Summary

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THE PARTNERS

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Small fuel cell system with cartridges for controlled hydrogen generation

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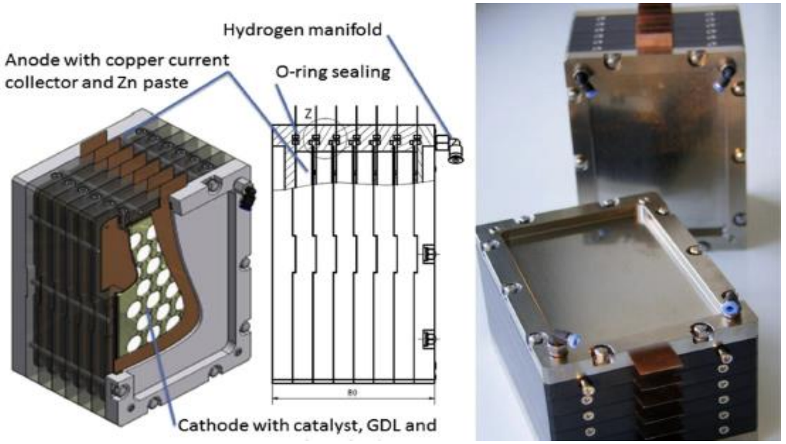

Zn2H2.com

- Hydrogen storage research started in 2000 at Eldat (Israel)
- Developed proprietary IP for metal ion management, charging methods, electrolytes
- Operated in stealth mode for over 15 years and recently filed key patents for the technology
- Founded German subsidiary in 2022 to become an active member of the European Hydrogen and Energy Storage Research community

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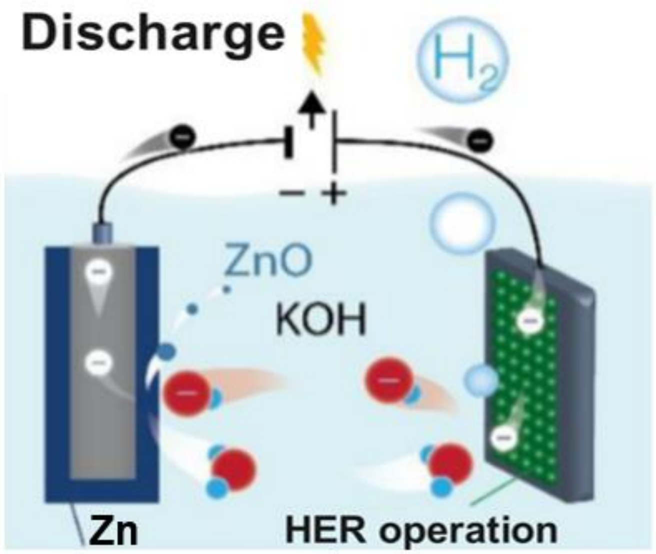
INTRODUCTION



charge (ZnO->Zn)	Reaktion (Edukte; Produkte)	Potential [V]
cathode (-)	$ZnO + H_2O + 2e^- \rightarrow Zn + 2OH^-$	$E_0 = -1{,}26$
	$ZnO + H_2O + 2OH^- \rightarrow Zn(OH)_4^{2-}$	
	$Zn(OH)_4^{2-} + 2e^- \rightarrow Zn + 4OH^-$	
anode (+)*	$2OH^- \rightarrow 1/2\ O_2 + H_2O + 2e^-$	$E_0 = 0{,}4$
		$\boldsymbol{E_{0\_Cell} = 1{,}66}$
Possible electrolysis during charge	reaction	potential [V]
cathode (-)	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	$E_0 = -0{,}83$
anode (+)*	$2OH^- \rightarrow 1/2\ O_2 + H_2O + 2e^-$	$E_0 = 0{,}4$
		$\boldsymbol{E_{0\_Cell} = 1{,}23}$

discharge (Zn->ZnO)	reaction	potential [V]
anode (-)	$Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^-$	$E_0 = -1{,}26$
	$Zn + 4OH^- \rightarrow Zn(OH)_4^{2-} + 2e^-$	
	$Zn(OH)_4^{2-} \rightarrow ZnO + H_2O + 2OH^-$	
cathode (+)*	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	$E_0 = -0{,}83$
		$\boldsymbol{E_{0\_Cell} = 0{,}43}$

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SYSTEM COMPARISON WITH ELECTROLYSER

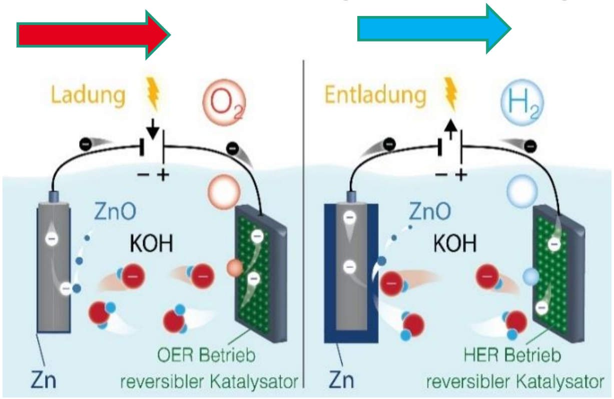
Zn-H2 storage

Step one:

generating O_2

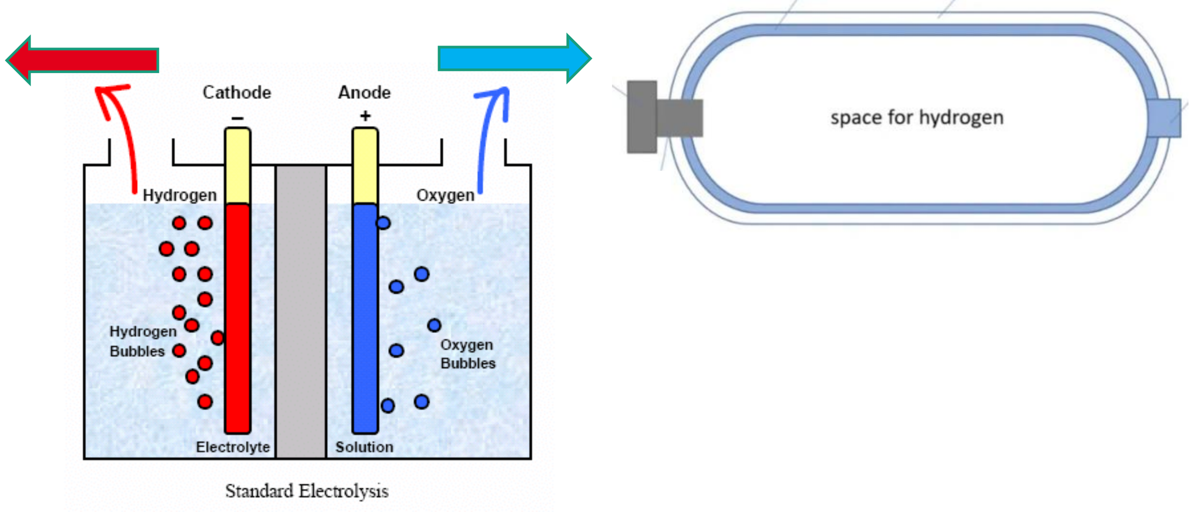
Step two:

generating H_2



- Energy is stored in form of deposited Zn
- Hydrogen is released when needed

Electrolyzer + hydrogen tank



- Hydrogen is produced when electricity is available
- Energy is stored in form of pressurized hydrogen

TRADITIONAL HYDROGEN STORAGE EFFICIENCY

Power to gas round trip efficiency of electricity storage is rather low

	Storage efficiency [% LHV H_2] [1,2]	Round trip efficiency of electricity storage [3]
Compressed hydrogen (700 bar)	85 %	33 %
Liquefied hydrogen	<= 70 %	< 27 %
Metal hydride	64-69 % (Mg_2Ni) 84-86 % ($LaNi_5$)	25 – 33 %
Ammonia	5 – 67 %	2 – 26 %
liquid organic hydrogen carriers (LOHC)	62-72 %	24 – 28 %

→ In comparison, the Zn-H2 system achieves an efficiency of more than 50% for the storage of electricity.

[1] Sanghun Lee, „Comparative Energy Economic Studies on Hydrogen Energy Storage Technologies“, The European Electrolyser & Fuel Cell Forum, July 4-7 2023, Lucerne, Switzerland

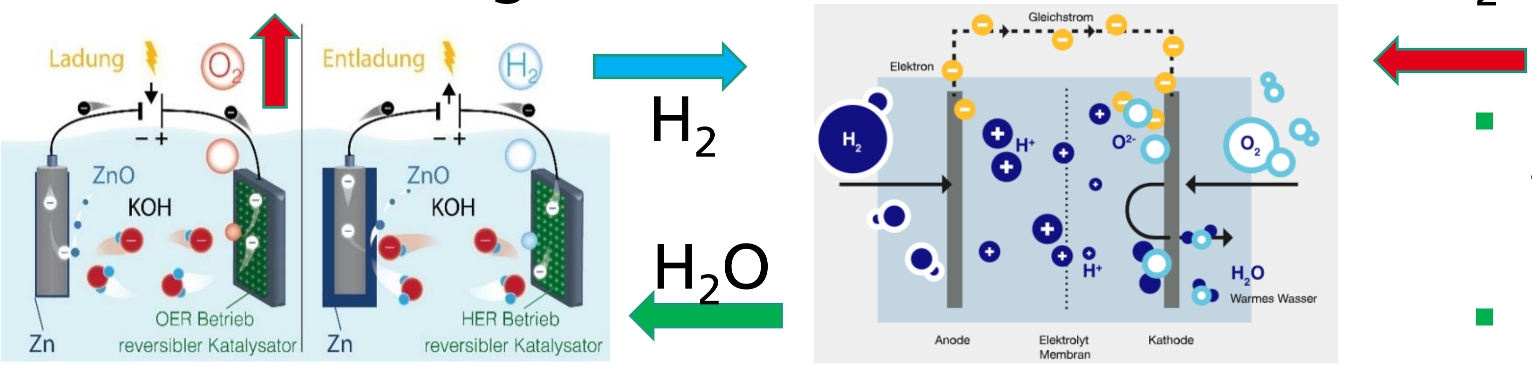
[2] S. Lee, T. Kim, G. Han, S. Kang et al. "Comparative energetic studies on liquid organic hydrogen carrier: A net energy analysis", Renewable and Sustainable Energy Reviews 150 (2021) 111447

[3] assuming 68% electrolyser efficiency, 57% fuel cell efficiency

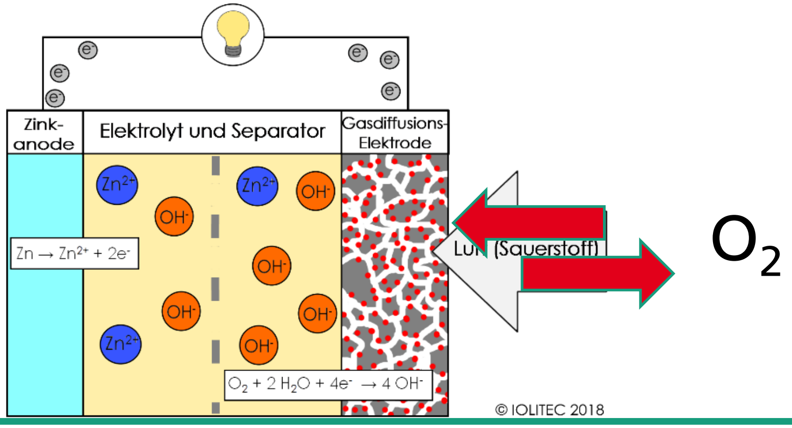
SYSTEM COMPARISON WITH RECHARGEABLE ZINC AIR BATTERY

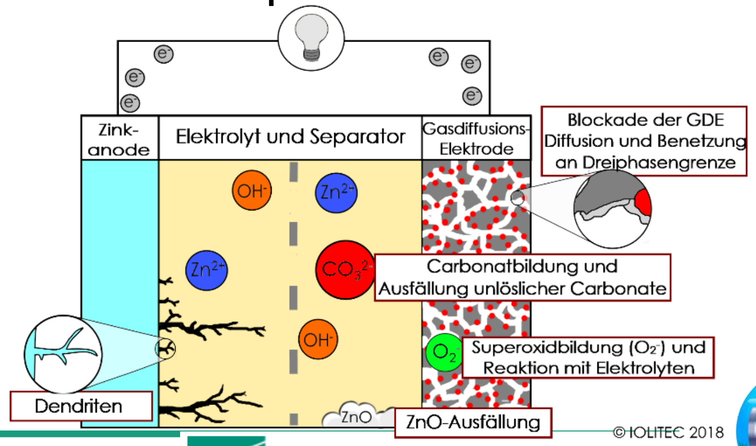
Zn-H2 storage

Fuel cell



- In combination with a fuel cell the system resembles a zinc air battery
- Rechargeable zinc air batteries are characterized by many unsolved problems





SYSTEM COMPARISON WITH ZINC AIR BATTERY

Zn-H2 storage

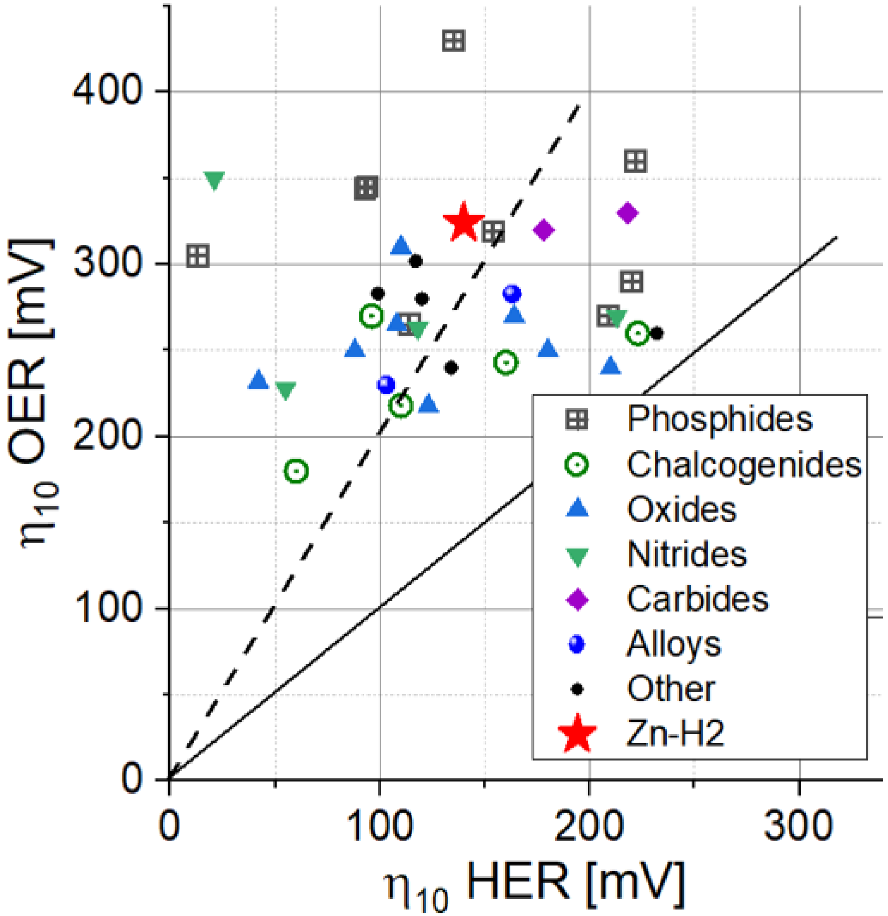
- Simple and robust electrochemical cell: only two steel substrates and KOH/ZnO electrolyte
- No separator, no gas diffusion layer, no ORR reaction, low cost metal alloy catalyst
- For round trip electricity storage additional components are required: fuel cell, gas drying, water supply, power electronics

Rechargeable zinc air

- One system – a rechargeable battery
- No other external components
- Lower TRL level, many issues like slow ORR, complex gas diffusion layer with many degradation mechanisms, direct access to the ambient air, CO_2 poisoning

→ High TRL level of the Zn-H2 system, only engineering problems have to be solved: cell and battery design, mass fabrication of large cells, gas and liquid management, power and control algorithms

EFFICIENCY OF THE ZN-H2 SYSTEM FOR ROUND TRIP ELECTRICITY STORAGE



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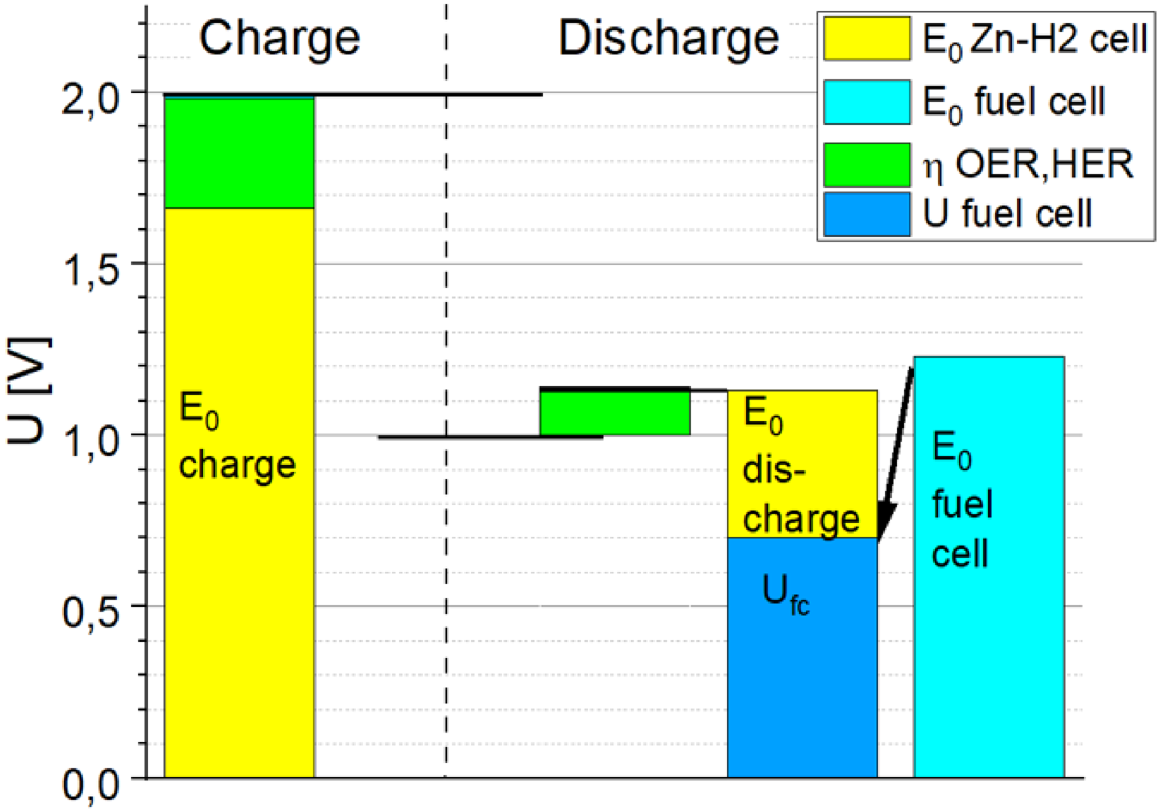

(Zn electrode overvoltages are not visible)

b)

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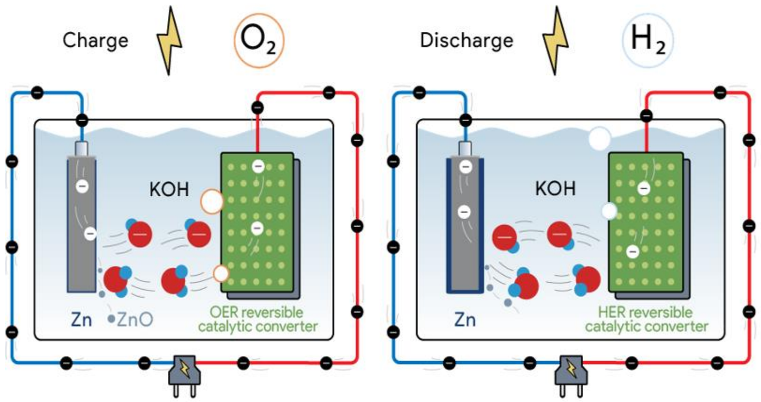
KEY INNOVATIONS ZN2H2

Why it works

- A robust, low cost catalyst electrode that can withstand the continuous switching between HER and OER and is unaffected by the zincate.
- Dedicated charging and controlled charge/discharge cycling algorithm
- Introduction of 100% DOD levels



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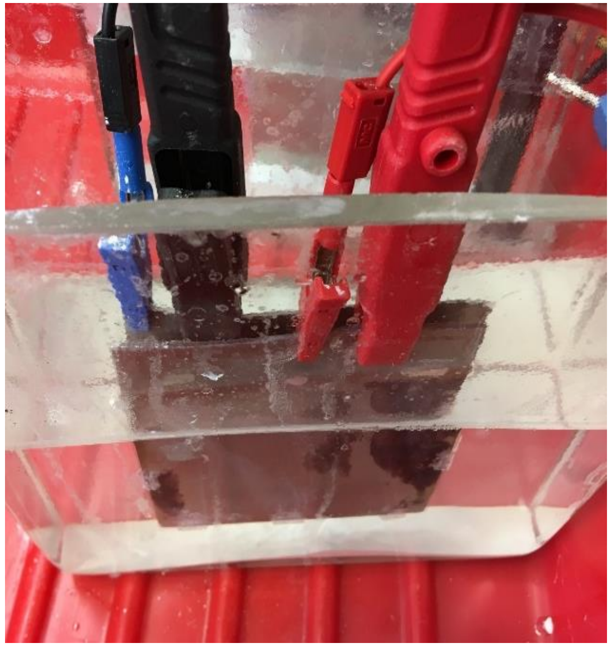
Full cell cycle testing: Test set-up



Large cells:

400 ml elctrolyte

6 mm electrode spacing

Electrode size: 50 x 70 mm^2

Catalyst: plated Ni alloy 4 µm

Substrate: low carbon steel or nickel foil

no separator

30 % KOH, saturated ZnO, T = 22 °C

small cells:

10 ml elctrolyte

3 mm electrode spacing

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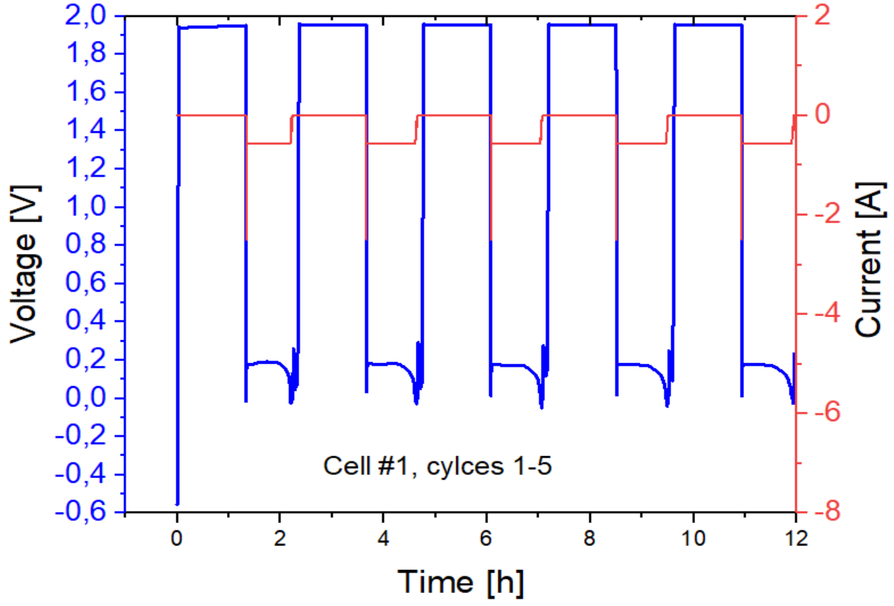
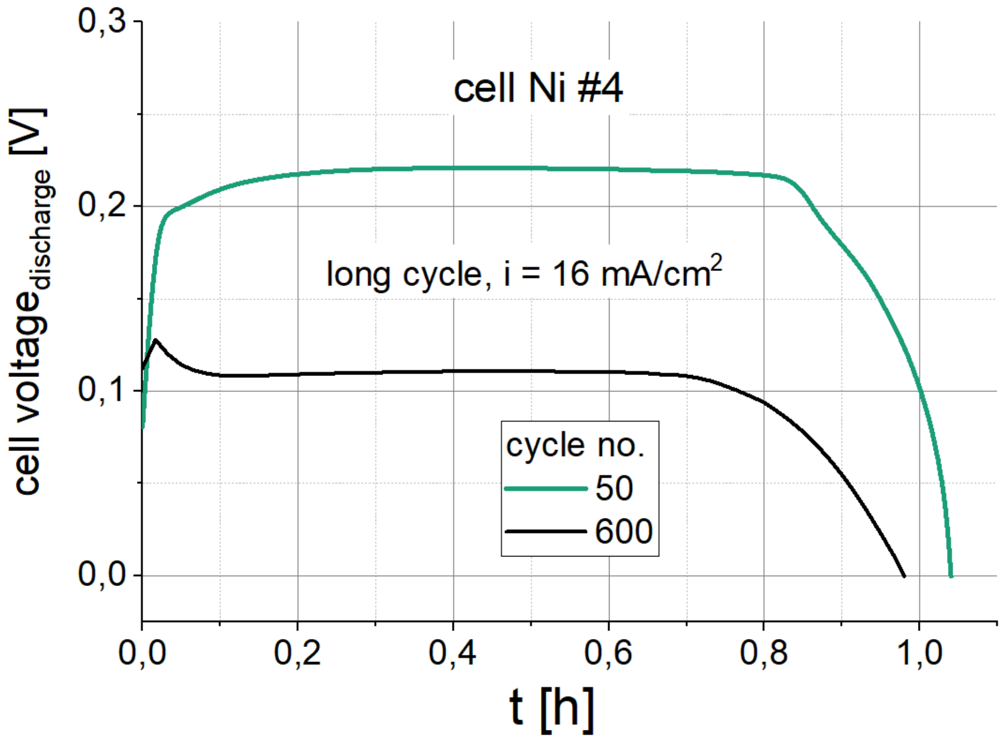
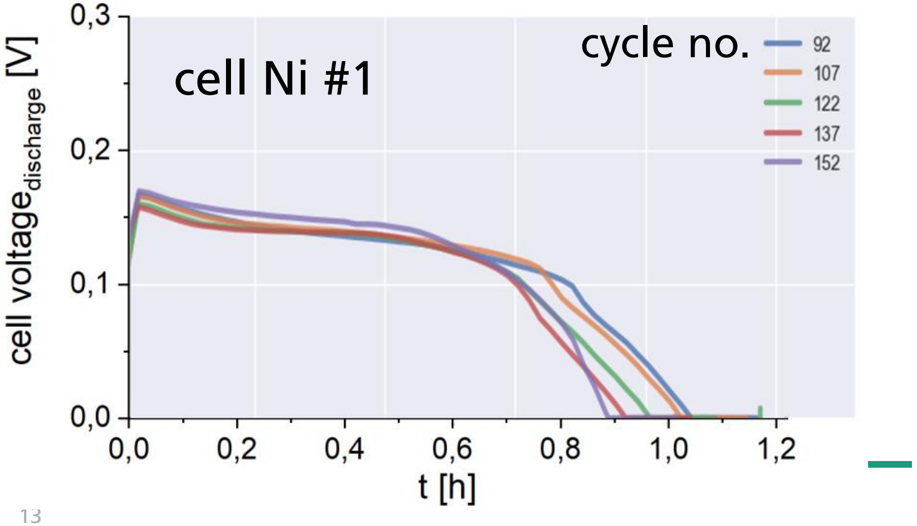
Cycle test parameters

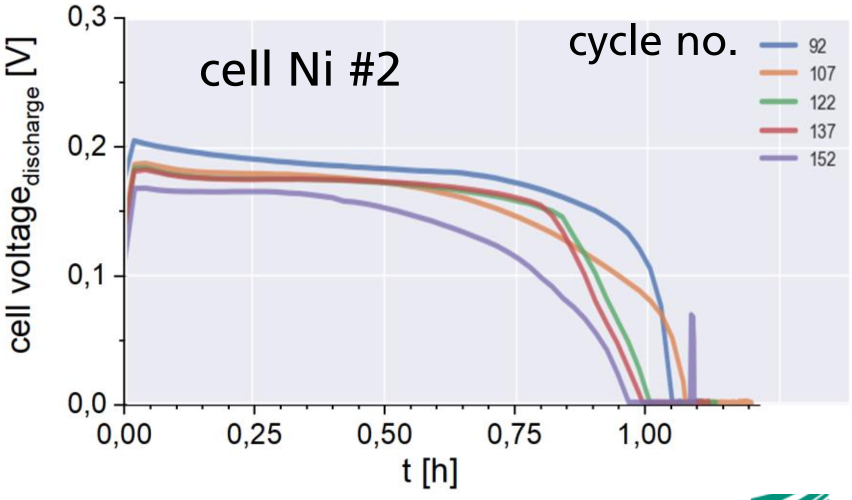
		short cycles	long cycles
Electrode loading	mAh/cm^2	0.17	17.0 large cells 8.0 small cells
Mean charge current	mA/cm^2	3.4	11
Charge limit voltage	V	2.3	2.3
Discharge current	mA/cm^2	3.4	16
Discharge limit voltage	V	0	0
Depth of discharge	%	-	100
small cell samples		Ni-2	Ni-1, Ni-3
large cell samples		Ni #3, Fe #1, Fe #2	Ni #1, Ni #2, Ni #4, Ni #5

Typical voltage profile









discharge voltages

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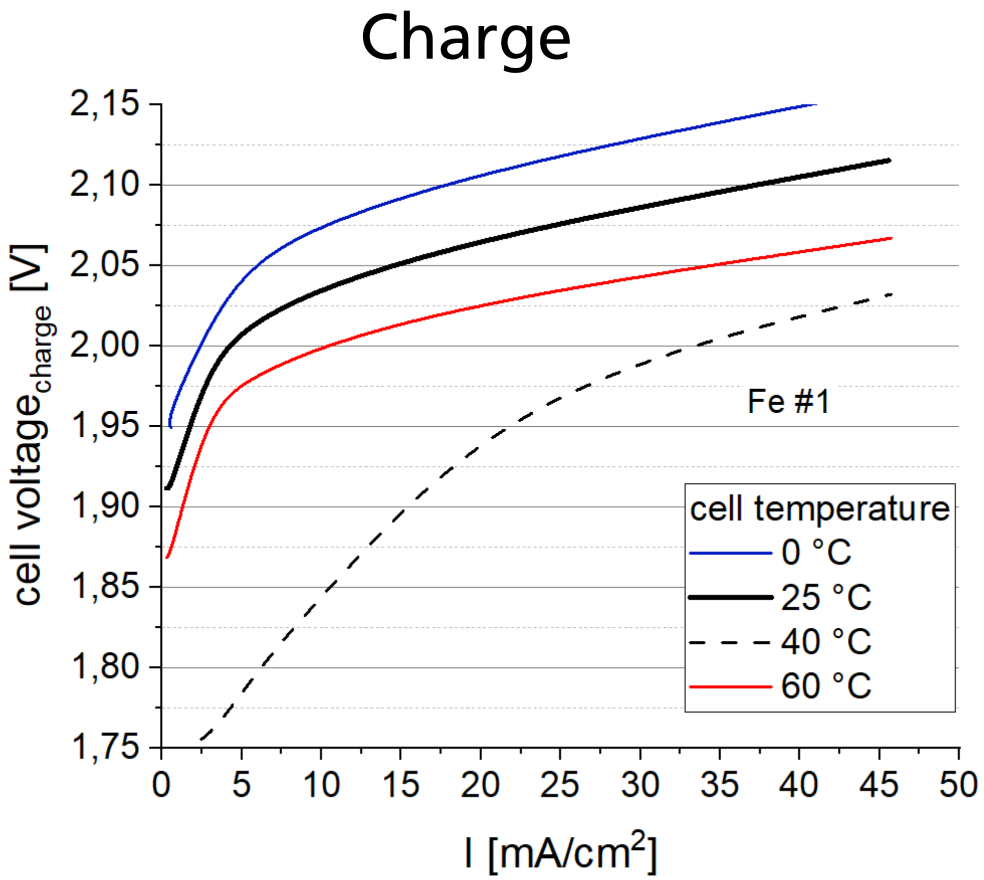
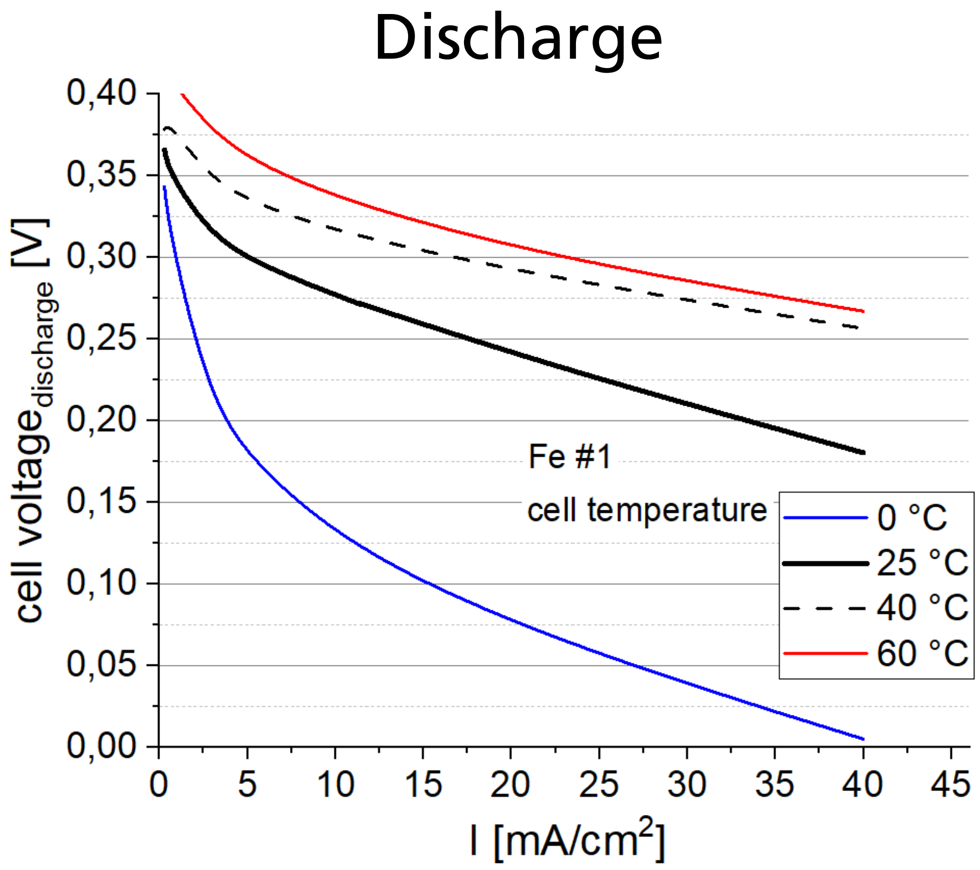
Initial U/I curves, influence of temperature





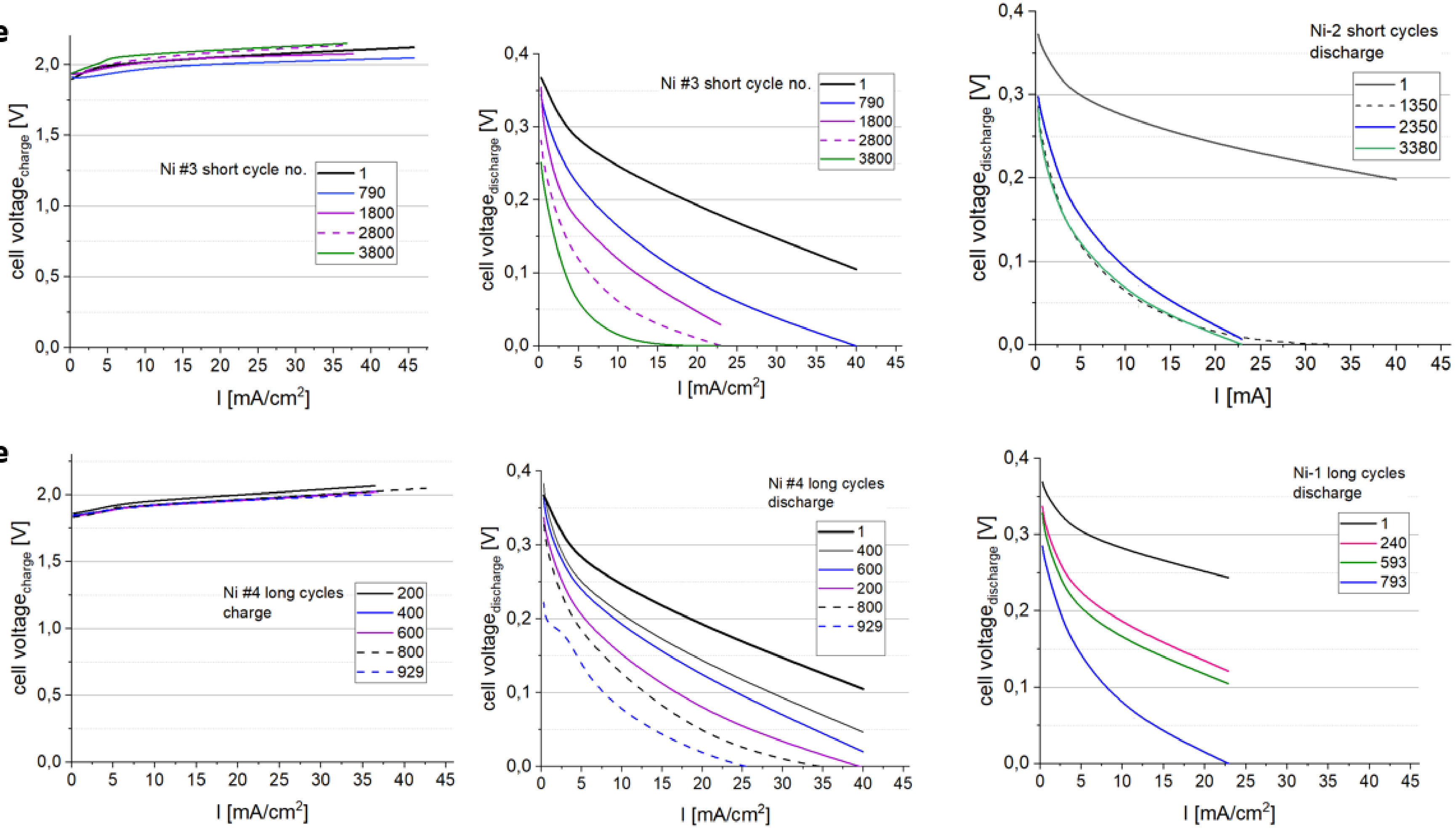
Large cells

V/I curves as function of cycles

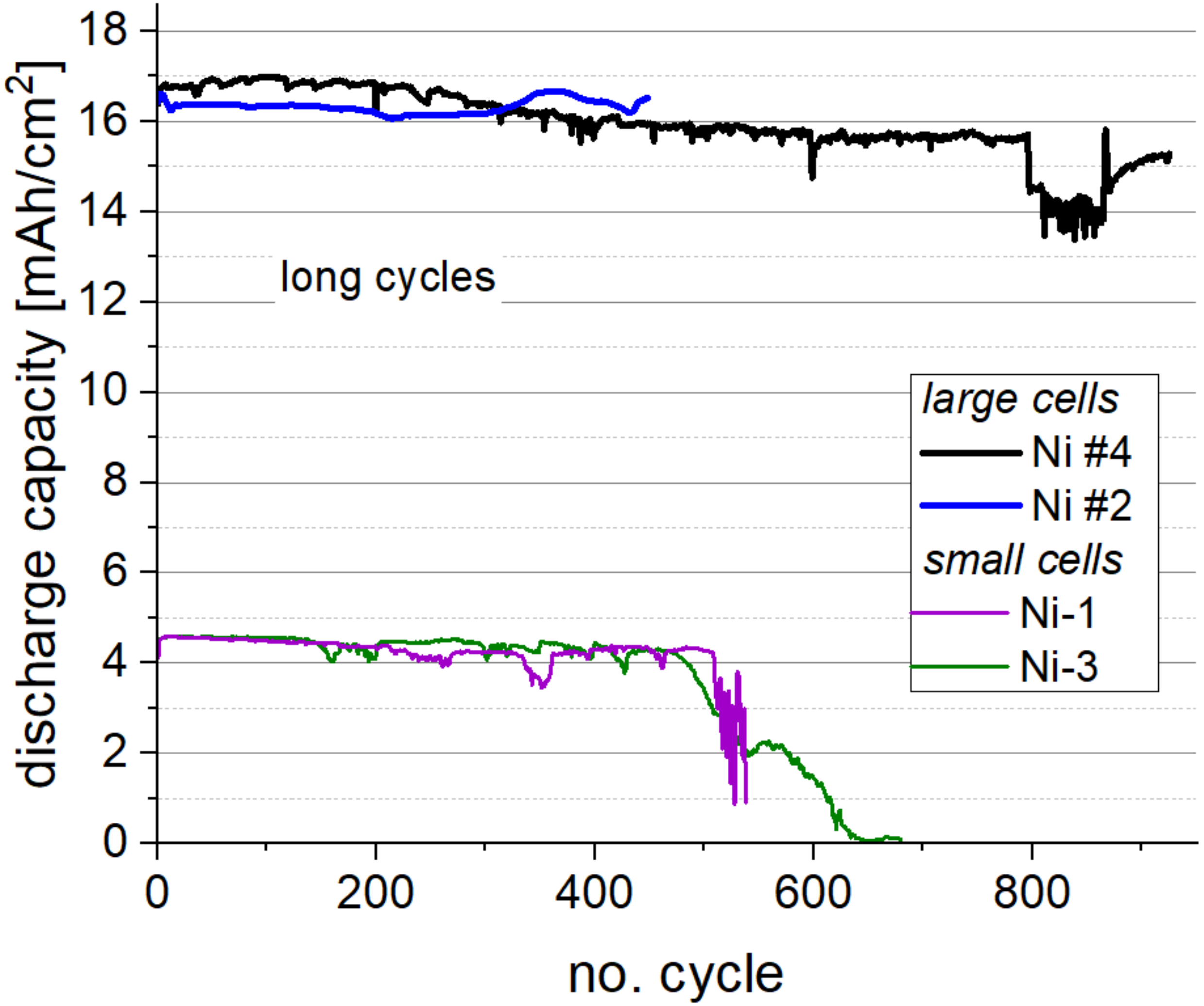
large cell | small cell

short cycle

long cycle



Discharge capacity as function of **long cycles**



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Summary of cycle testing: cumulative capacity

	large cells		small cells	
	no. cycles	cumulative capacity [Ah/cm^2]	no. cycles	cumulative capacity [Ah/cm^2]
short cycles	**7000**	**0.9**	**3800**	**0.65**
long cycles	**925** **665**	**14.7** **10.1**	**793** **546**	**3.3** **1.9**

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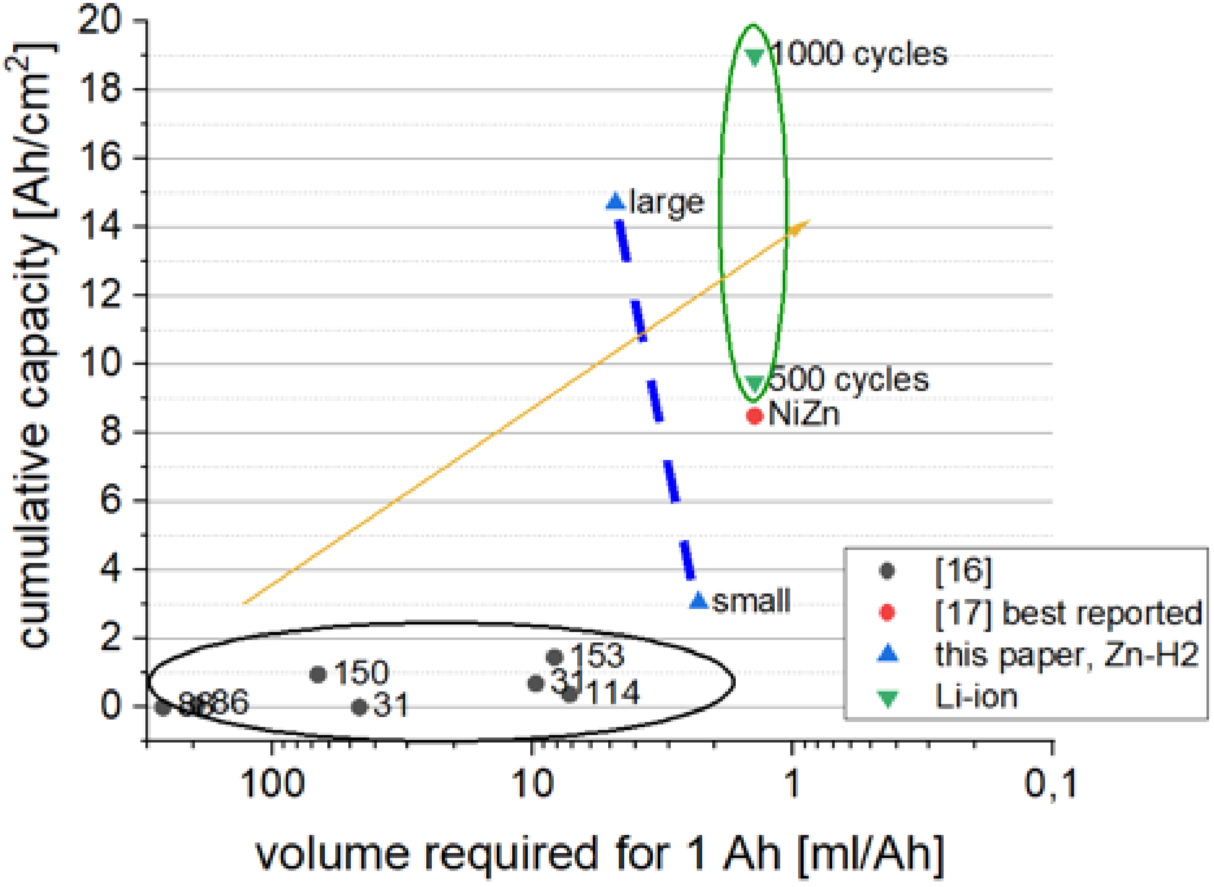
CAPACITY COMPARISON TO RECHARGEABLE ZN, LI-ION



[16] H. Luo, B. Liu, Z. Yang, Y. Wan, C. Zhong, The Trade-Offs in the Design of Reversible Zinc Anodes for Secondary Alkaline Batteries, 2021 Electrochemical Energy Reviews https://doi.org/10.1007/s41918-021-00107-5

[17] Z.P. Arkhangelskaya, A. V. Krasnobryzhii, T. B. Kasyan, Processes in a Nickel-Zinc battery with a negative Electrode conatining a calcium Hydroxide Additive. Russian Journal ofApplied Chemistry,Vol. 78, No. 3,2005, pp. 4253429

ZN DEPOSITION - CHARGING

DC-charging

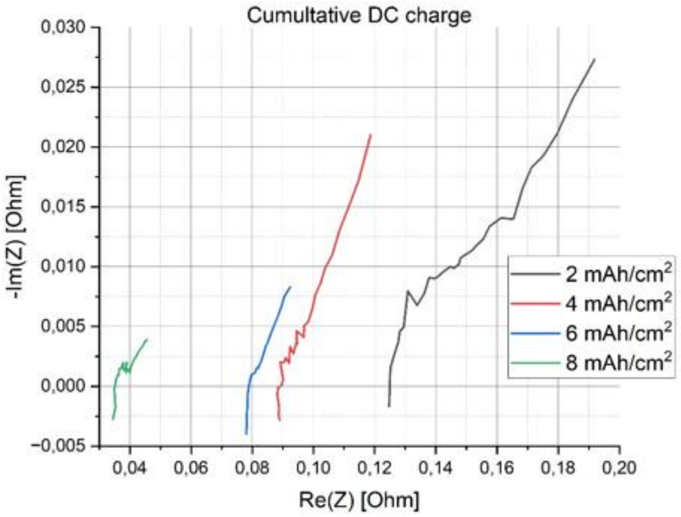
- only up to ca. 2 mAh/cm^2 possible, (I <=20 mA/cm^2)
- loose Zn powder and mossy zinc at higher capacity, significant reduction in impedance

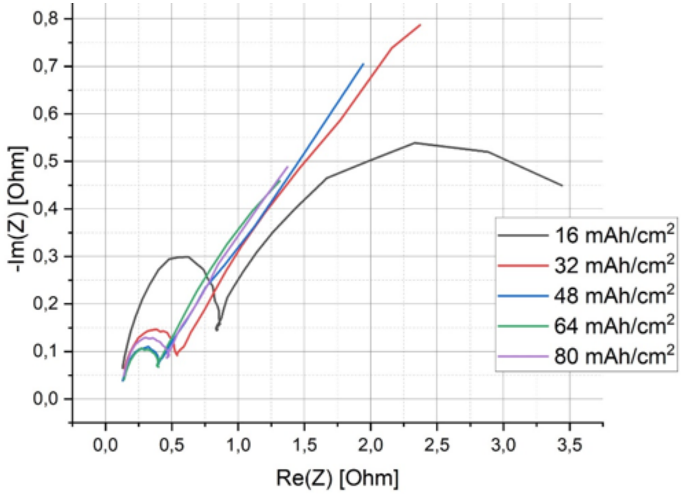
Pulsed charging ZnO-paste

- The starting in ZnO paste requires reduced current density/duty cycle, ca. 10 mA/cm^2
- Up to 270 mAh/cm^2 was achieved
- No major reduction in impedance

Pulsed deposition in zincate electrolyte

- Higher current density/duty cycle possible, ca. 40 mA/cm^2
- Up to 80 mAh/cm^2 was tested
- No major reduction in impedance





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HIGH CAPACITY ZINC CHARGING

60 mAh/cm²

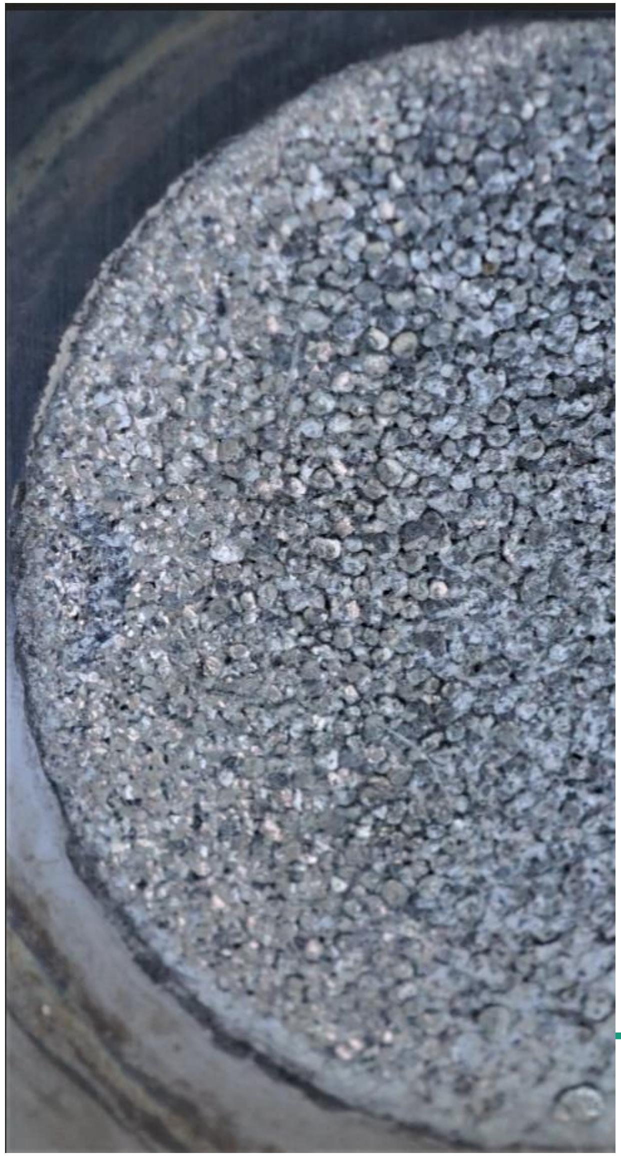
190 mAh/cm²

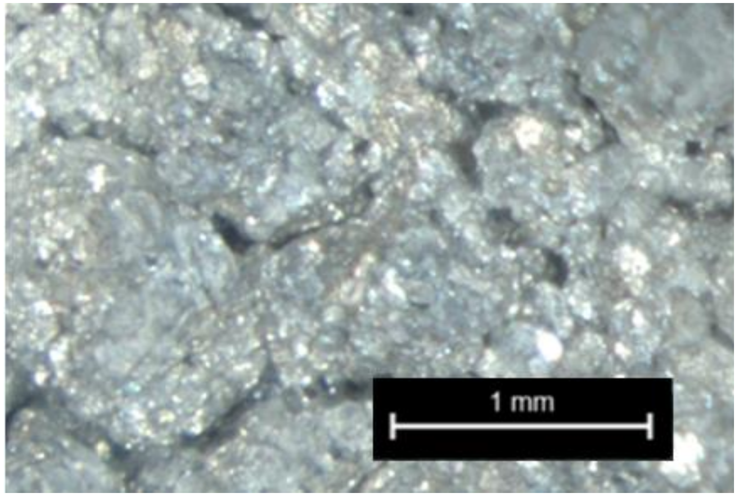
270 mAh/cm²

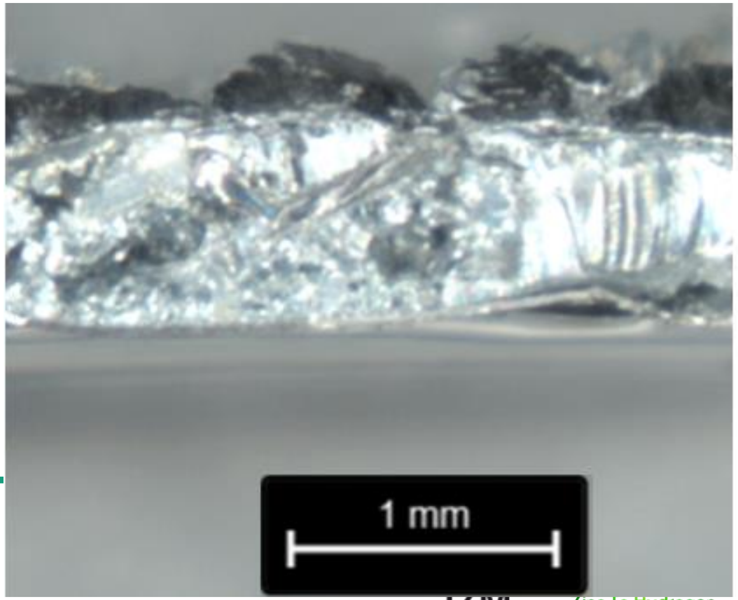
30 mm diameter

- Deposition start from zinc oxide paste
- Even several hundred µm thick deposits result in solid, well adhered, metallic shimmering zinc
- Large boulder grains
- No dendrites, no mossy zinc

High capacity zinc charging (270 mAh/cm^2)







SUMMARY

- A novel electrochemical energy storage system was tested, featuring a robust, simple cell design and very low material cost
- Catalyst stability has been demonstrated for more than 900 cycles at a capacity of 17 mAh/cm^2
- Several thousand HER/OER cycles, HER degradation is more dominant than OER degradation
- High capacity density >200 mAh/cm^2 and cumulative capacity > 10Ah/cm^2
- The overall efficiency of electricity storage of 50%, much higher than for power-to-gas systems
- A better theoretical understanding is to be expected from the BMBF-funded project Zn-H2
- The electrochemical storage cell has a high TRL level; engineering challenges remain

Thus, the Zn-H2 system could provide an early solution for storing energy to be used in the Energy Transition

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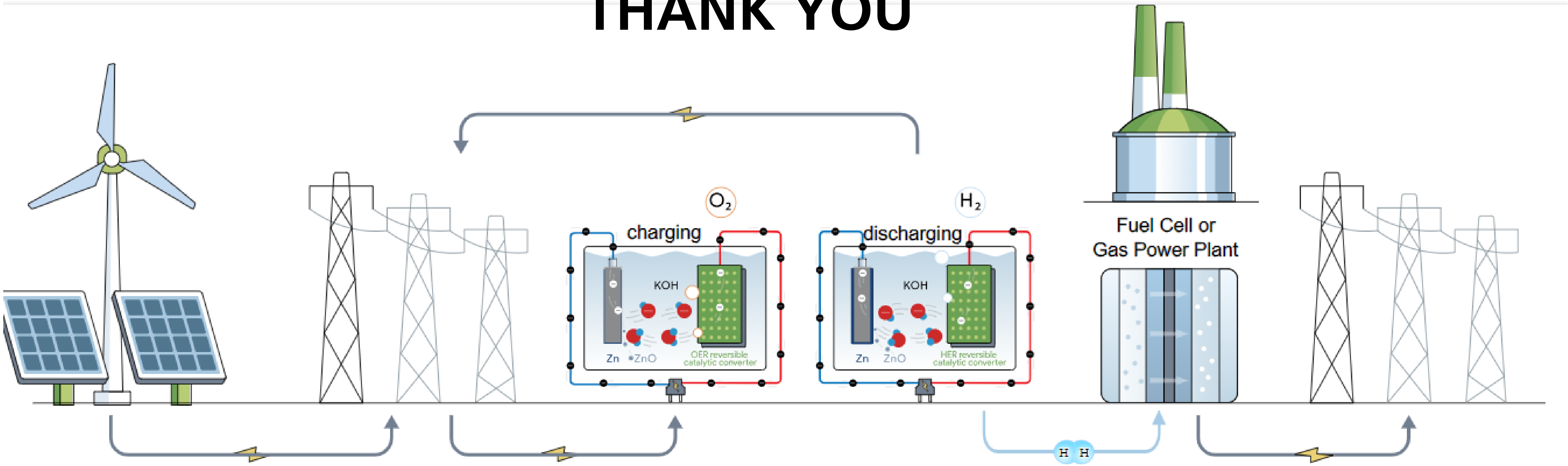
THANK YOU



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