A short history of flow battery research at Fraunhofer ICT

Nordic Flow Battery Autumn School, Turku, Finland, 2021

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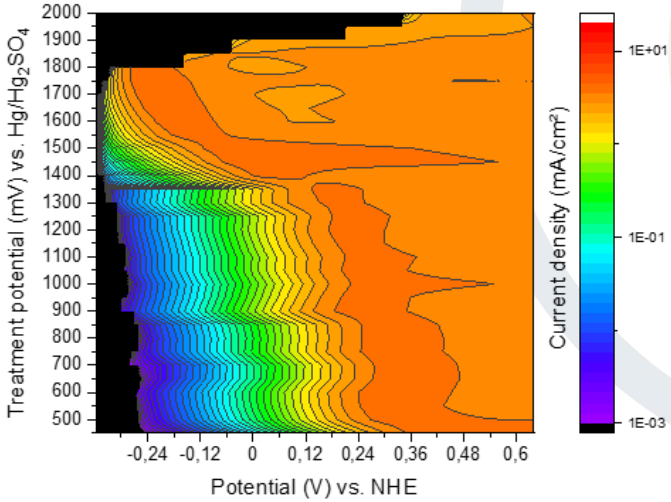
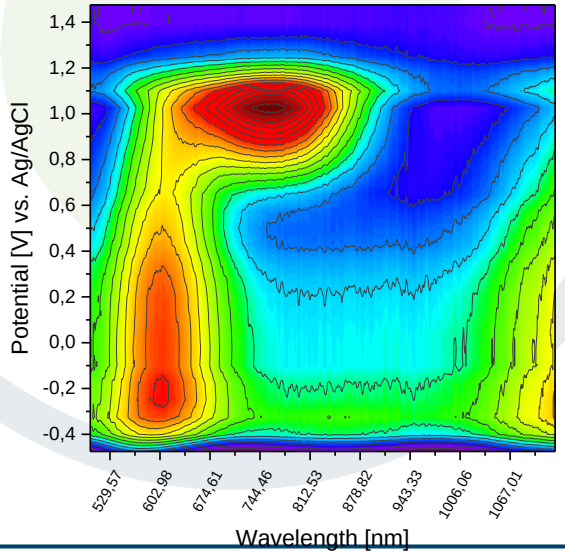
[2] German-Australian Alliance for Electrochemical Technologies for Storage of Renewable Energy, Mechanical and Manufacturing Engineering, University of New South Wales (UNSW), UNSW Sydney NSW 2052 Australia
[3] University of New South Wales (UNSW), UNSW Sydney NSW 2052 Australia

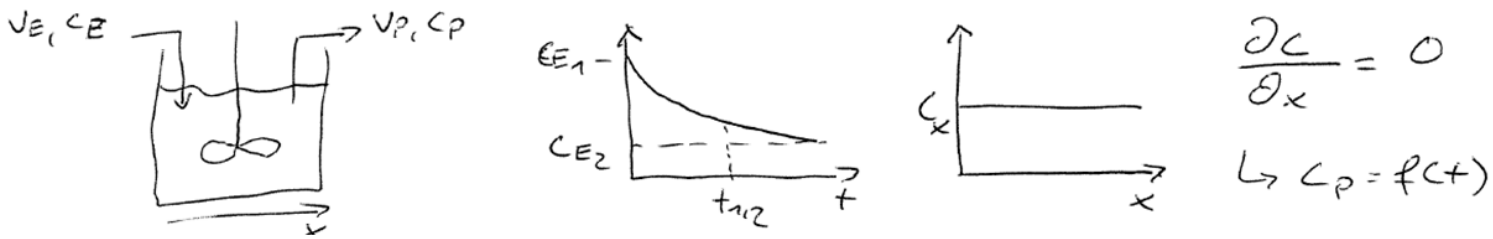




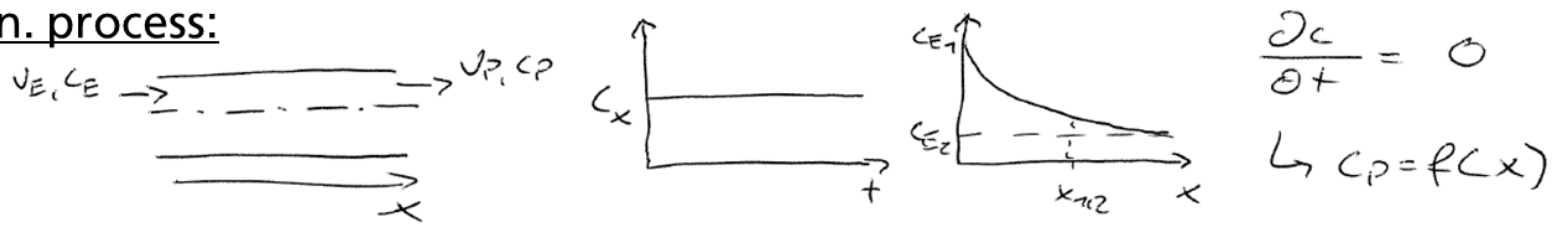
What is a Flow Battery?

- Arbitrary classical classification
- Thought experiments (flowing suspensions, reversible fuel cell, changing aggregate state, reversibility?)
  - Electrolysis, Galvanisation?
- Better: classification by basic process types

<u>Disc. process:</u>



<u>Contin. process:</u>



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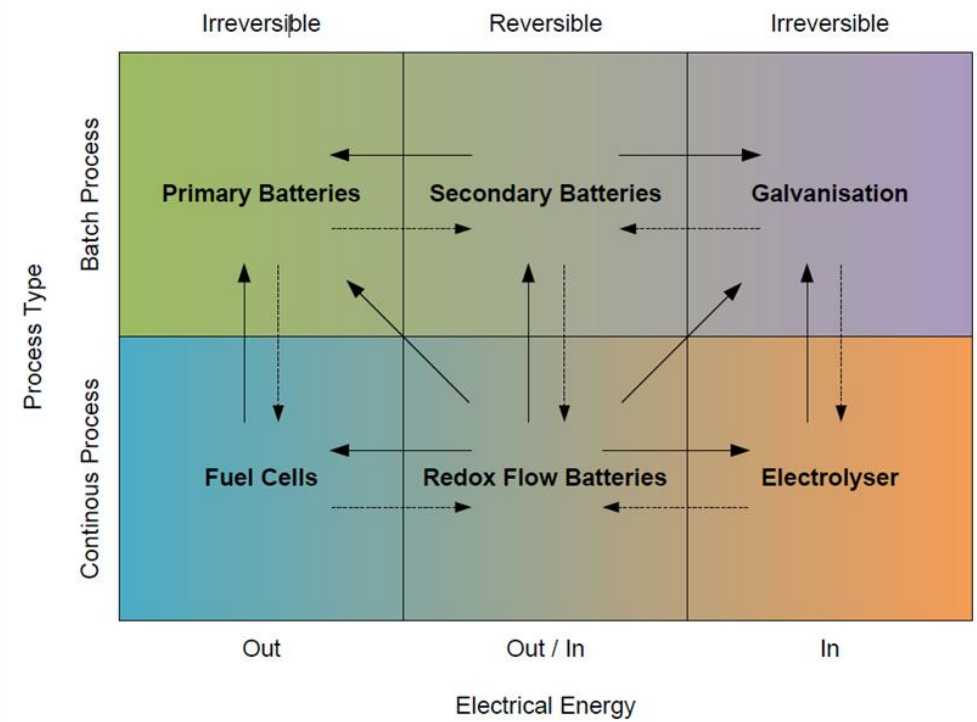
What is a Flow Battery?

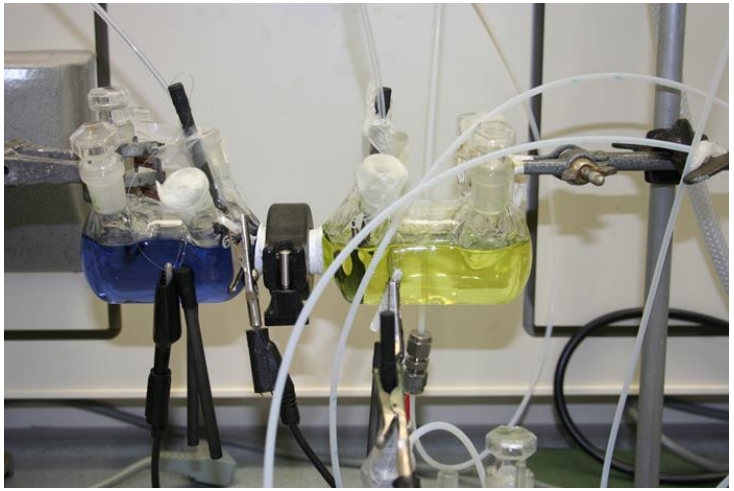


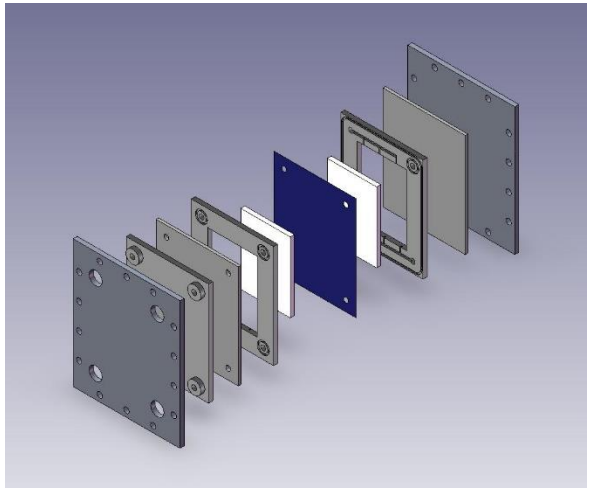
- Consequences:
  - Reversible fuel cells are RFBs
  - RFBS represent a kind highest form of electrochemical energy conversion, since they can immediately take any other form
  - Reversibility is diffuse - considering the actual use

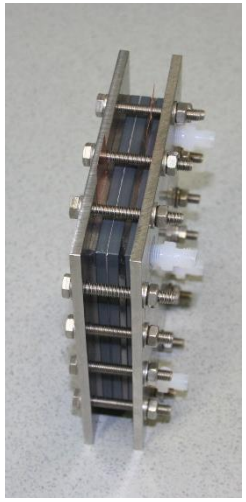
2007 - Fraunhofer MaVo AES

Fraunhofer Project "Marktorientierte Vorlaufforschung - Advanced Energy Storage"

- Study of different storage Technologies for different Szenarios
- ICT was responsible for electrochemical storage
- Not much public information available
- 1st to build a test cell and produce electrolyte to study behavior of different chemistries







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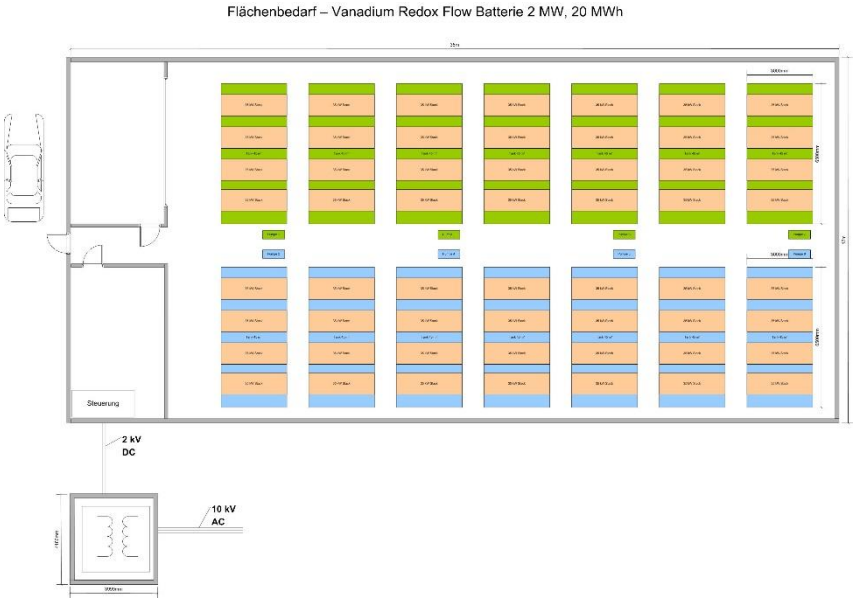
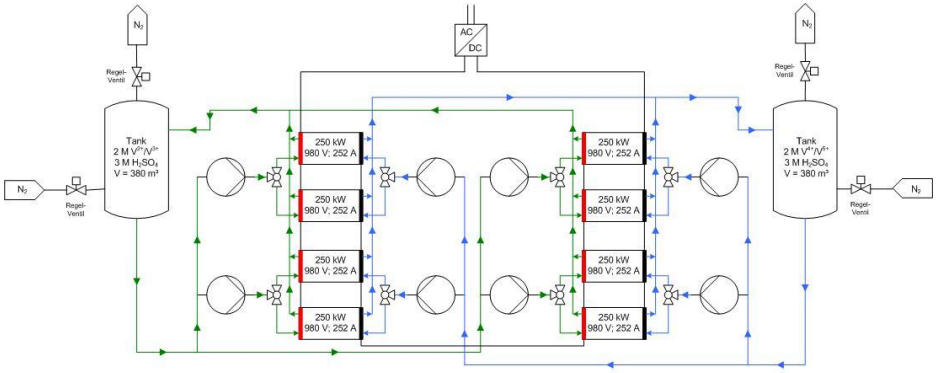
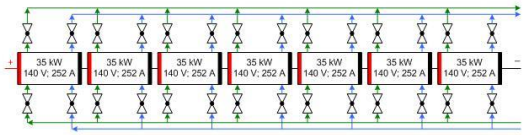
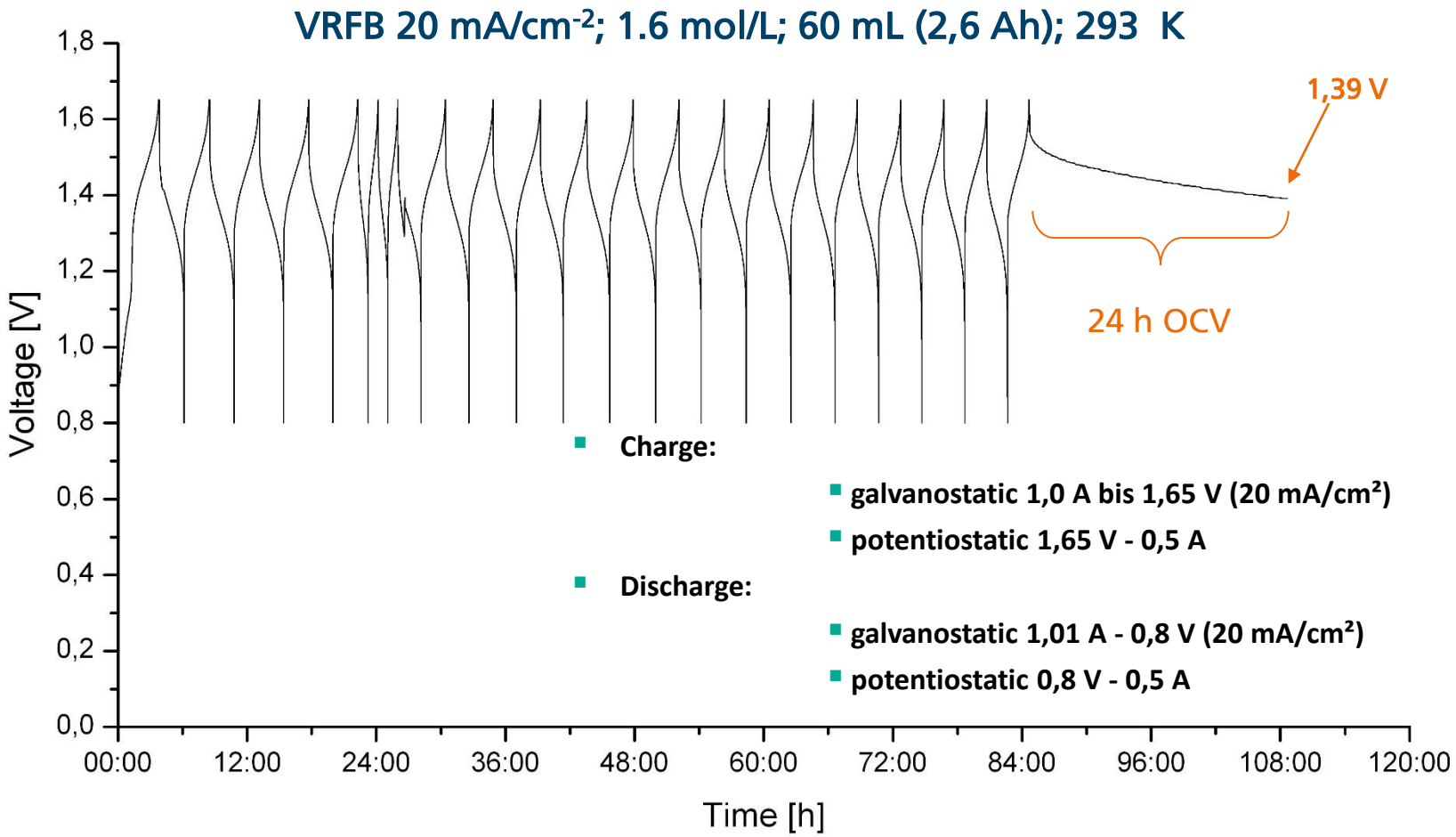
2008 - 2 MW Vanadium Flow Battery - Pre-Design



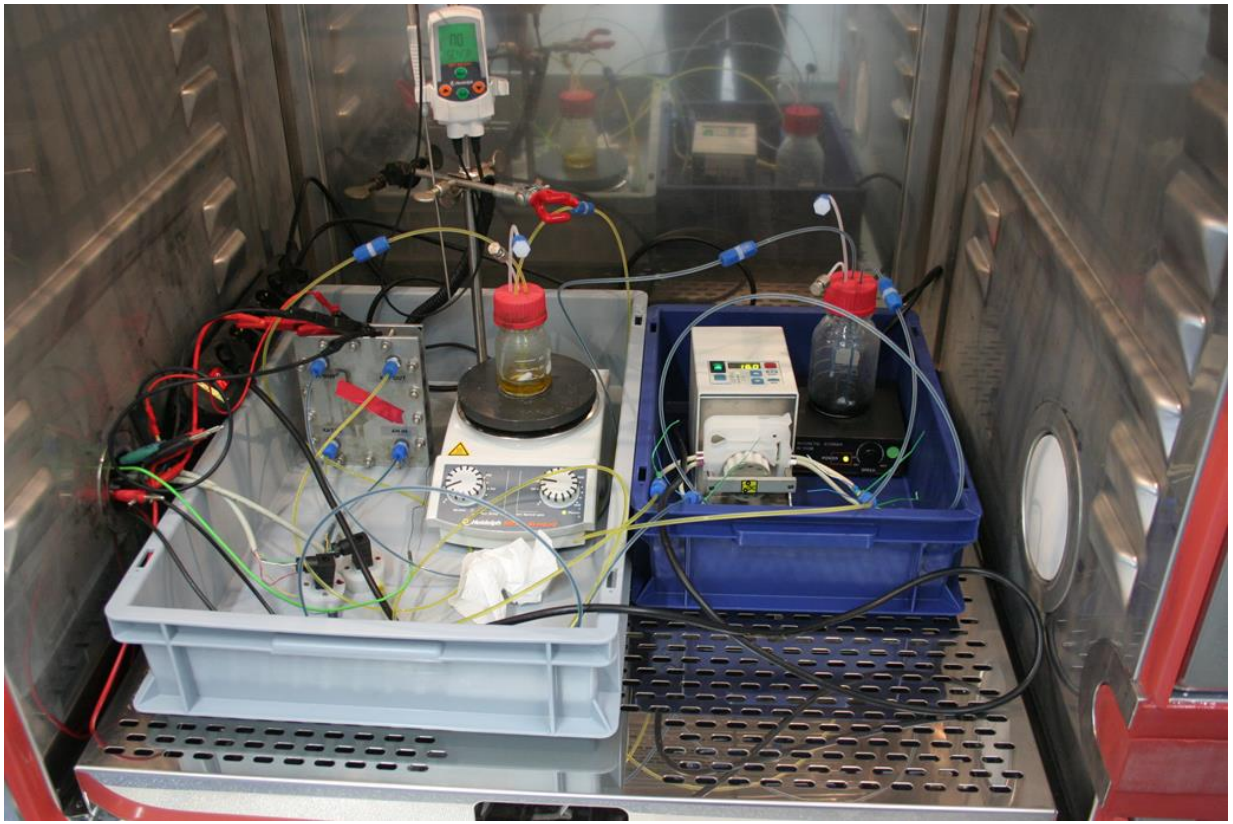




2008 - V/V Flow Battery



2008 - Fe/Cr Flow Battery



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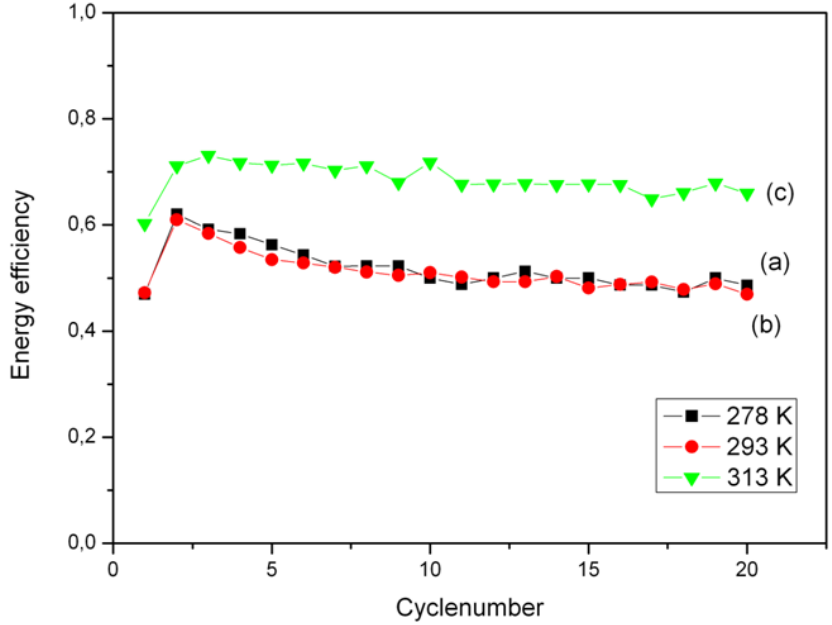
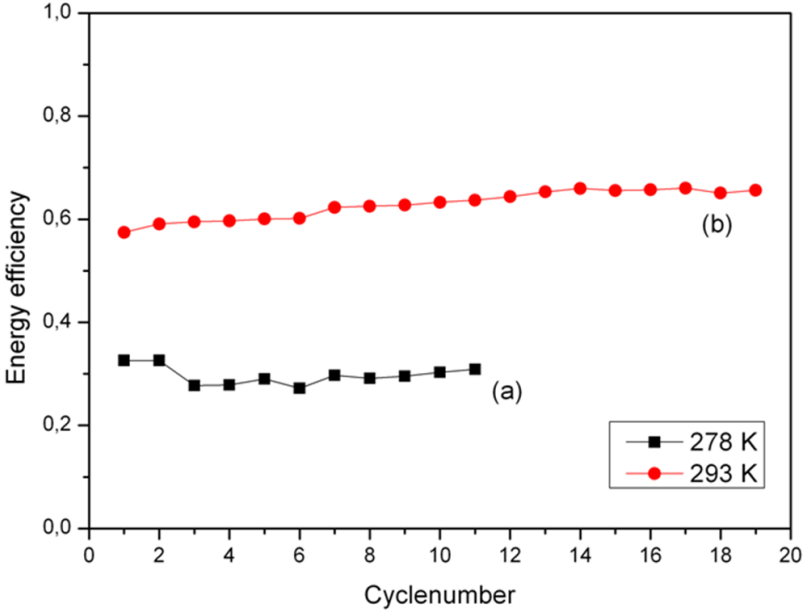
2008 - Fe/Cr, Zn/Br

Fe/Cr - FB (1 M, 20 mA/cm²)



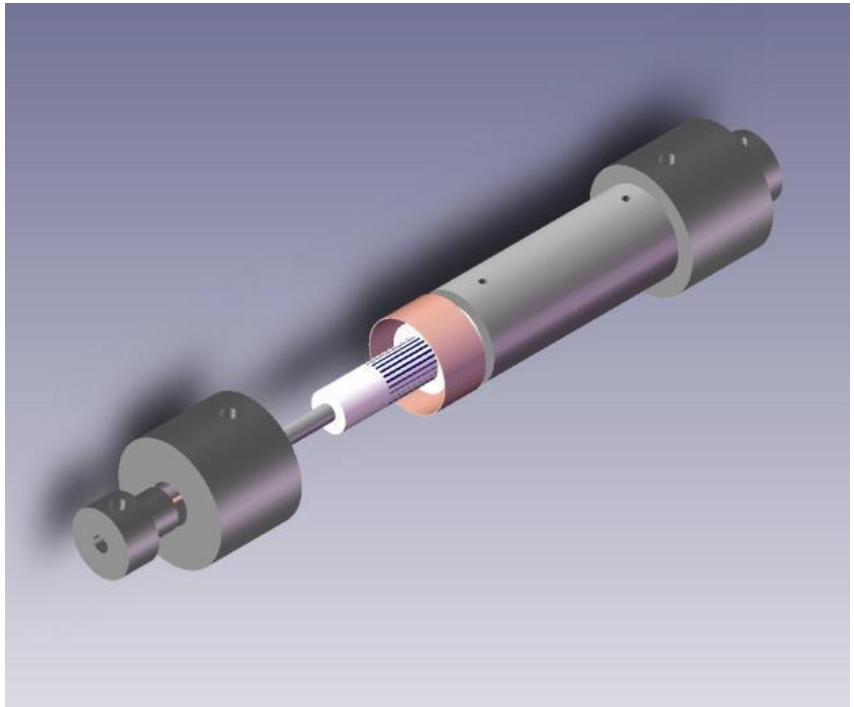
Zn/Br - FB (1 M, 20 mA/cm²)



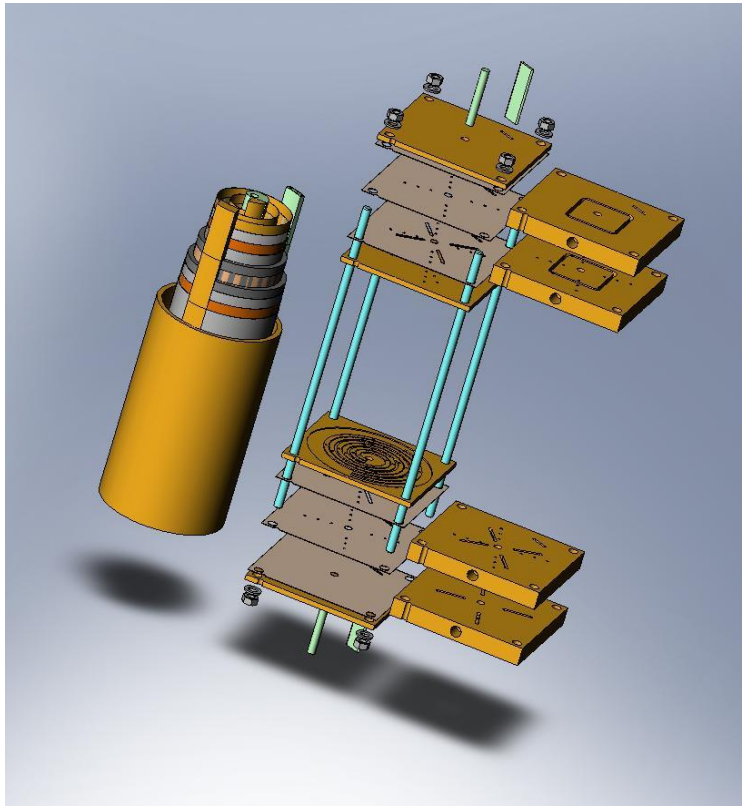
J. Noack, J. Tübke, BATTCON – International stationary battery conference, Florida, USA, 2009

2009 - Alternative cell designs

Tubular flow battery design



Spiral wound (swiss roll) design

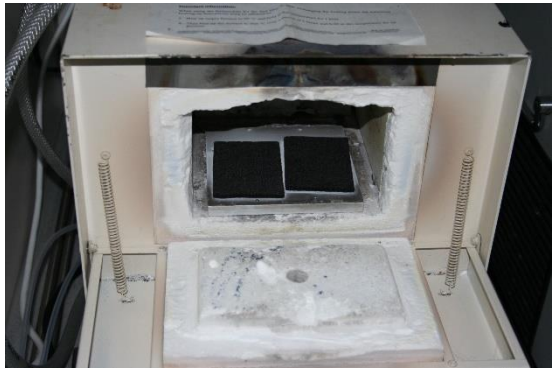


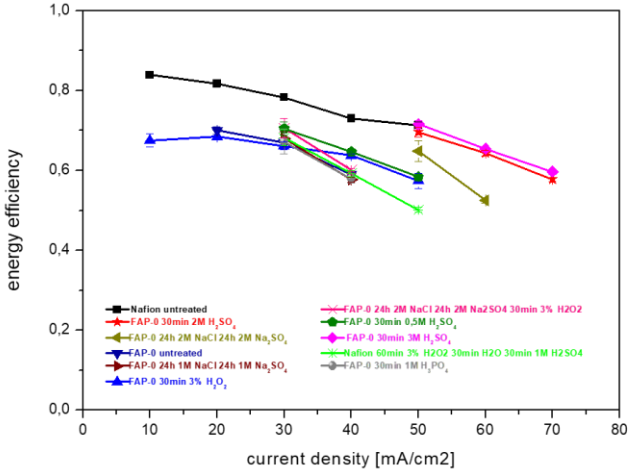
J. Noack, K. Rennebeck, L. Löwe, J. Tübke, International Symposium on Electrochemistry for Energy Conversion and Storage, International Society of Electrochemistry, Wuhan (Three Gorges), China, 2009

2009 - Treatment of materials for VFBs

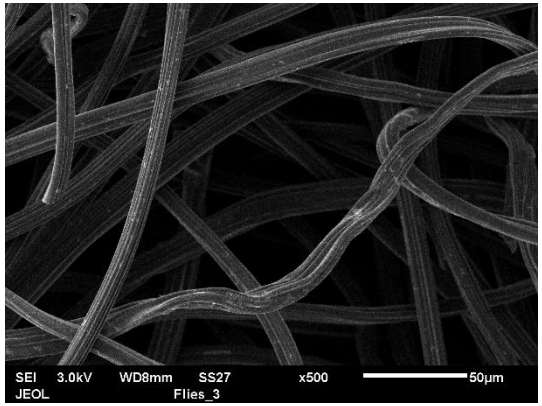
Acid treatment

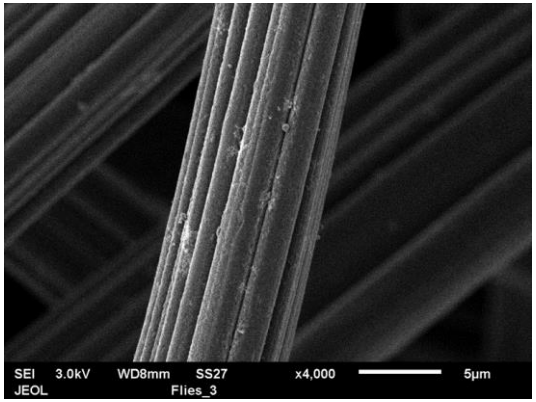
Heat treatment

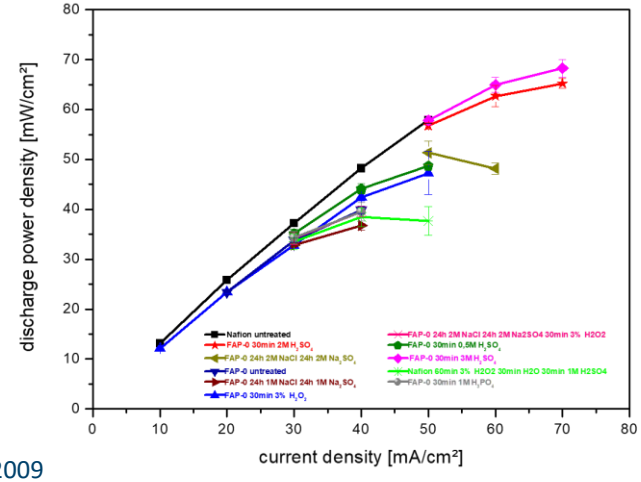




SEM of felt after 5h conc. H_2SO_4 cooking

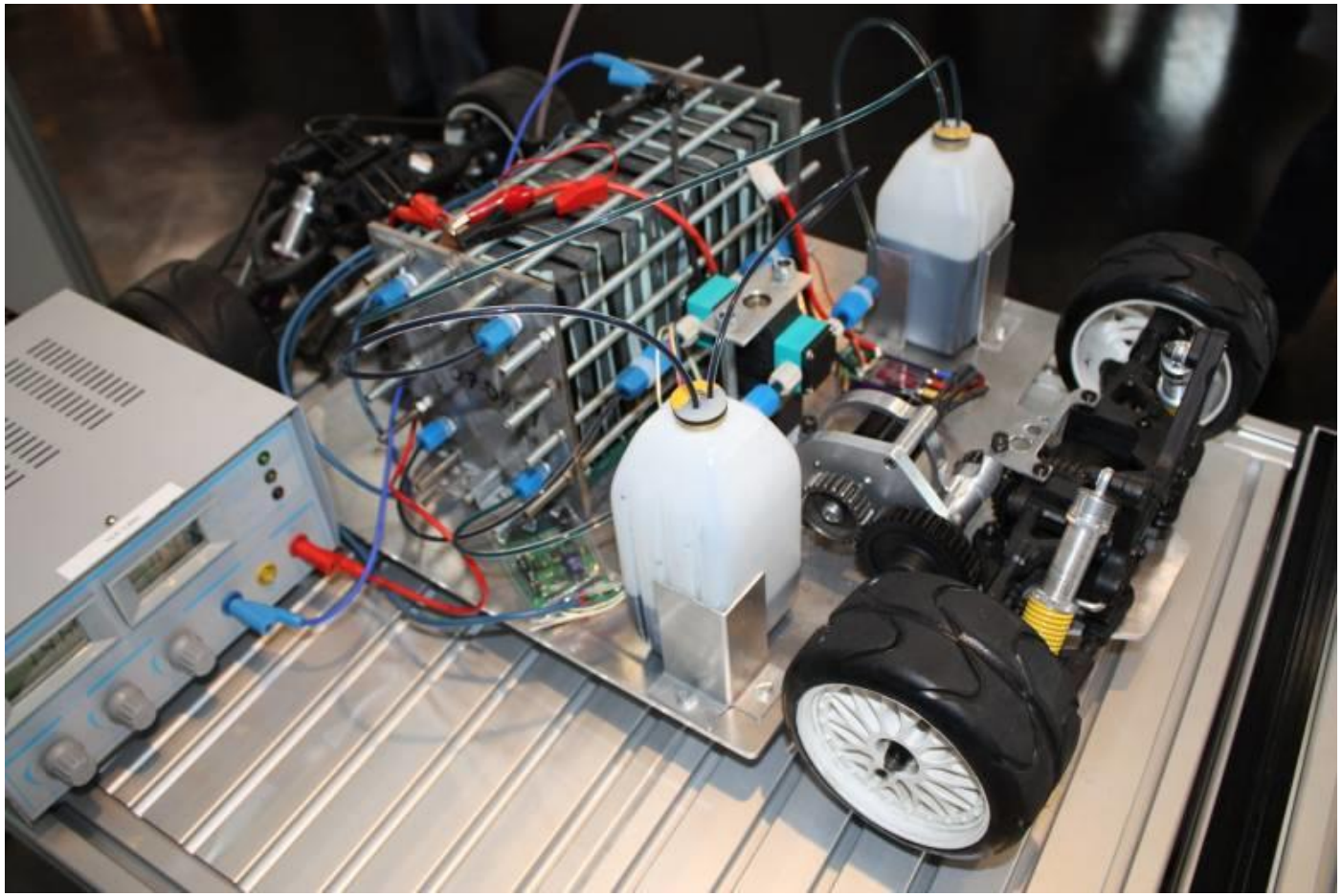






J. Noack, J. Tübke, Konferenzbeitrag, The Electrochemical Society, 216th Meeting, Vienna, Austria, 2009

2009 - VFB test car @ eCarTect 2009 Munich / Germany



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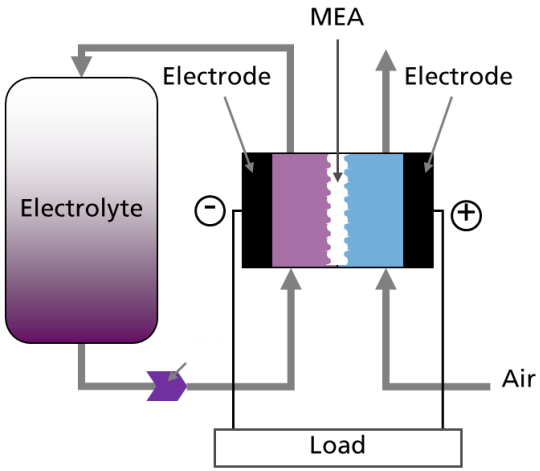
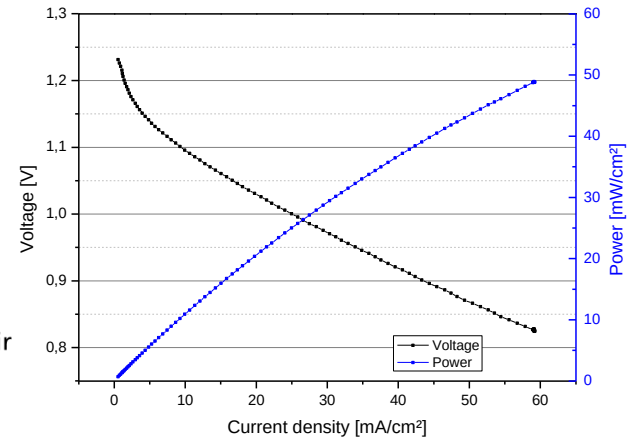
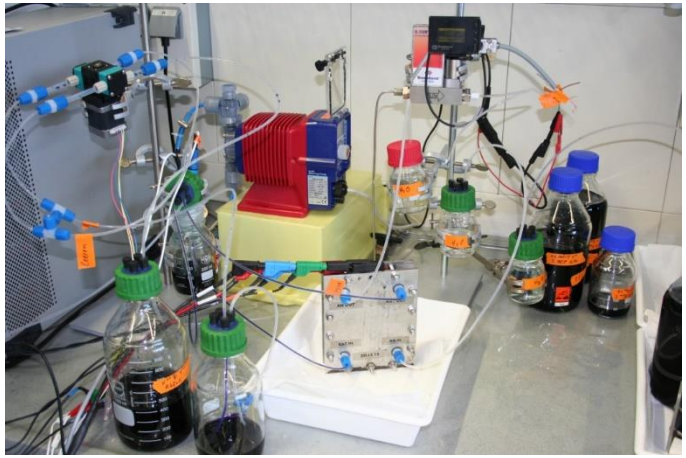
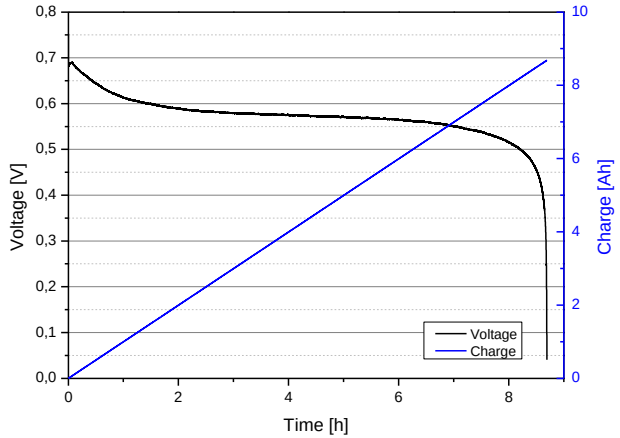
2009/2010 - Vanadium/Oxygen fuel cell (VOFC)







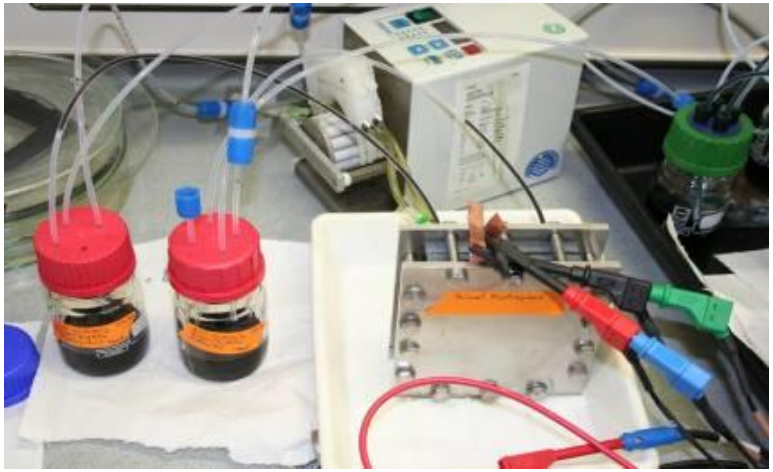


200 mL 80 mL/min1.6 M V^{2+}, 50 mL/min Air, 8.6 Ah, 25 mA/cm²

- 2 mg/cm² Pt 40 % C, NAFION® 117 (Baltic Fuelcells GmbH, Germany)
- 1.6 M V^{2+}, 2 M H_2SO_4, 0.05 M H_3PO_4 (Electrolytically produced by electroreduction of 0.8 M $VOSO_4$, 0.8 M $V_2(SO_4)_3$
- 40 cm² active area
- Graphite felt (GFA5, SGL-Carbon, Germany)
- Graphite composite bipolar plate (FU 4369, Schunk Kohlenstofftechnik GmbH, Germany)

J. Noack, C. Cremers, K. Pinkwart, J. Tuebke, Konferenzbeitrag, The Electrochemical Society, 218th Meeting, Las Vegas, USA, 2010

2010 - Organic Flow Batteries $V(Acac)_3$/Acetonitrile

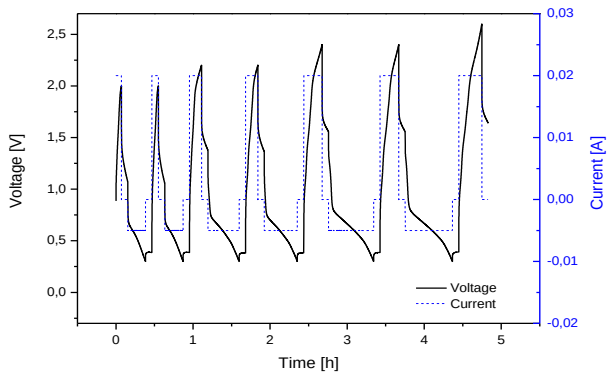


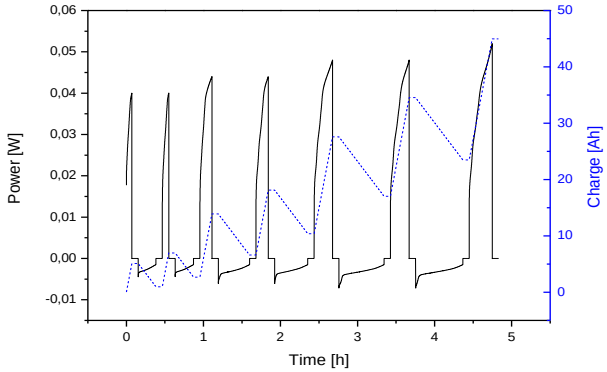
MICHIGAN MEMORIAL PHOENIX ENERGY INSTITUTE

UNIVERSITY OF MICHIGAN

- 10 cm² active area
- Scimat microporous separator
- 0.1 M V(Acac)3, 0.05 M TEABF4
- Acetonitrile

- 20 mA (2 mA/cm²) galvanostatic charge up to 2 V, 2.2 V, 2.4 V, 2.6 V
- 5 min OCV-Measurement
- 5 mA (0.5 mA/cm²) galvanostatic discharge down to 0.3 V





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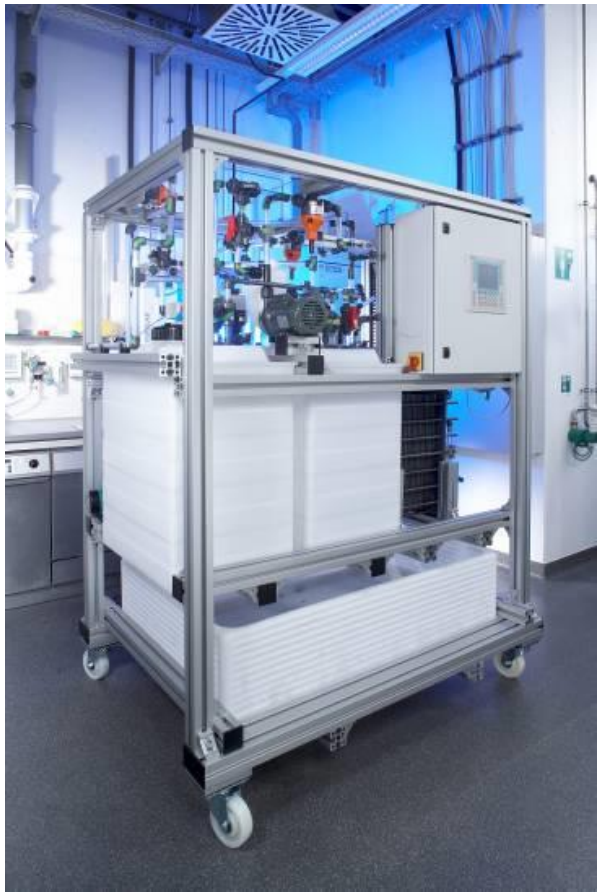
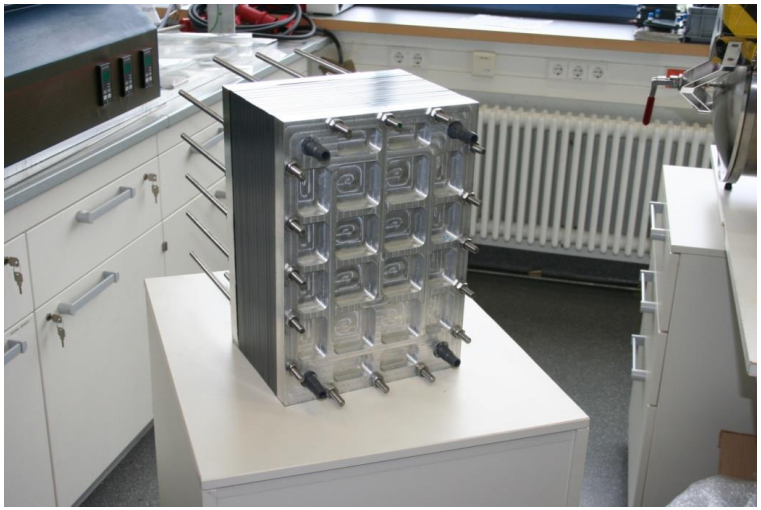
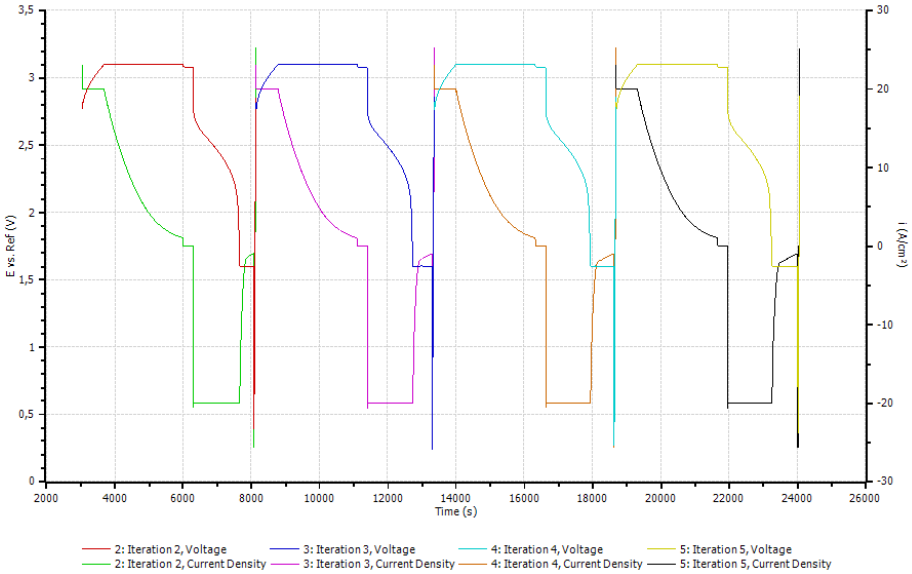
2010 - VFB kW class test system



2011 - VFB kW class stacks

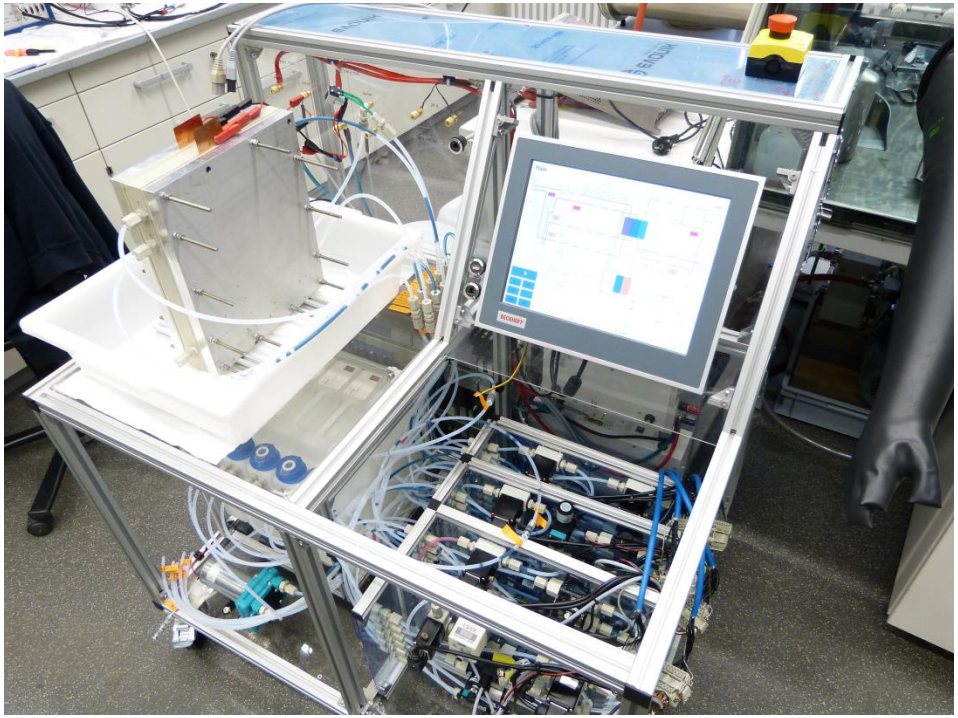


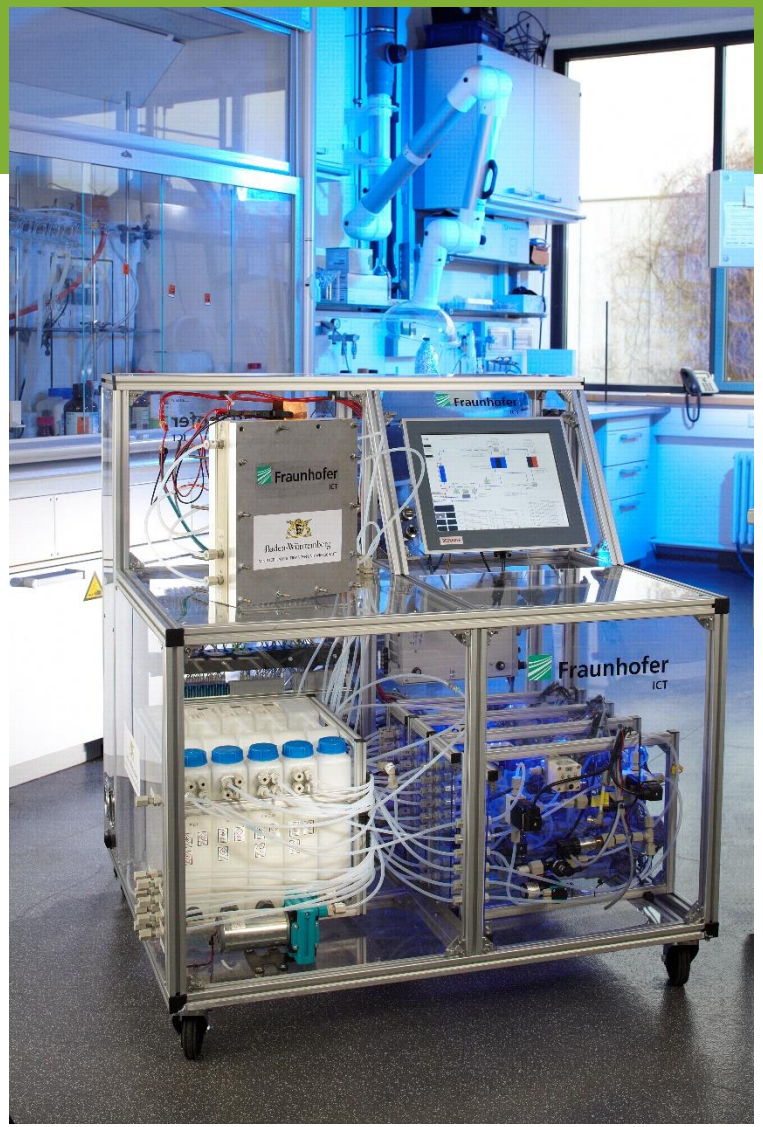


- 600 cm², 22 cells, 18 – 35 V
- Max. 60 A, 1,5 kW
- Simple stack design
- Simple assembly
- Process technologies for series production (Injection moulding of frames)

- Electrical tests two cell stack
- 30 mA/cm²
- Power: 40 – 50 W

2012 - VOFC kW class demonstrator





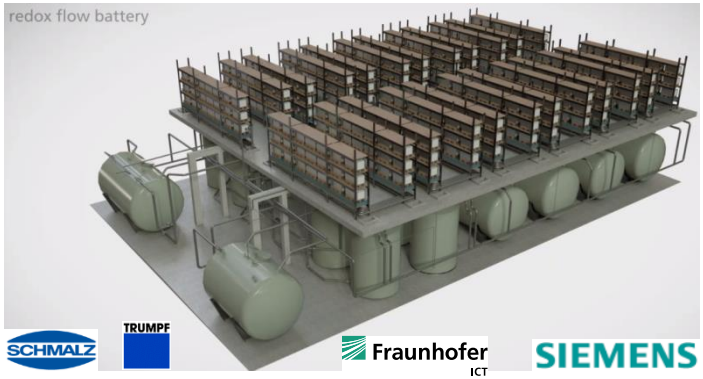
J. Noack, J. Tuebke, 3rd International Flow Battery Forum, Munich, Germany, 2012
J. Noack, T. Roth, M. Hihn, J. Tuebke, The 7th International Green Energy Conference & The DNL 1st Conference on Clean Energy, Dalian, China, 2012

VFB – Upscaling to 2 MW/20 MWh

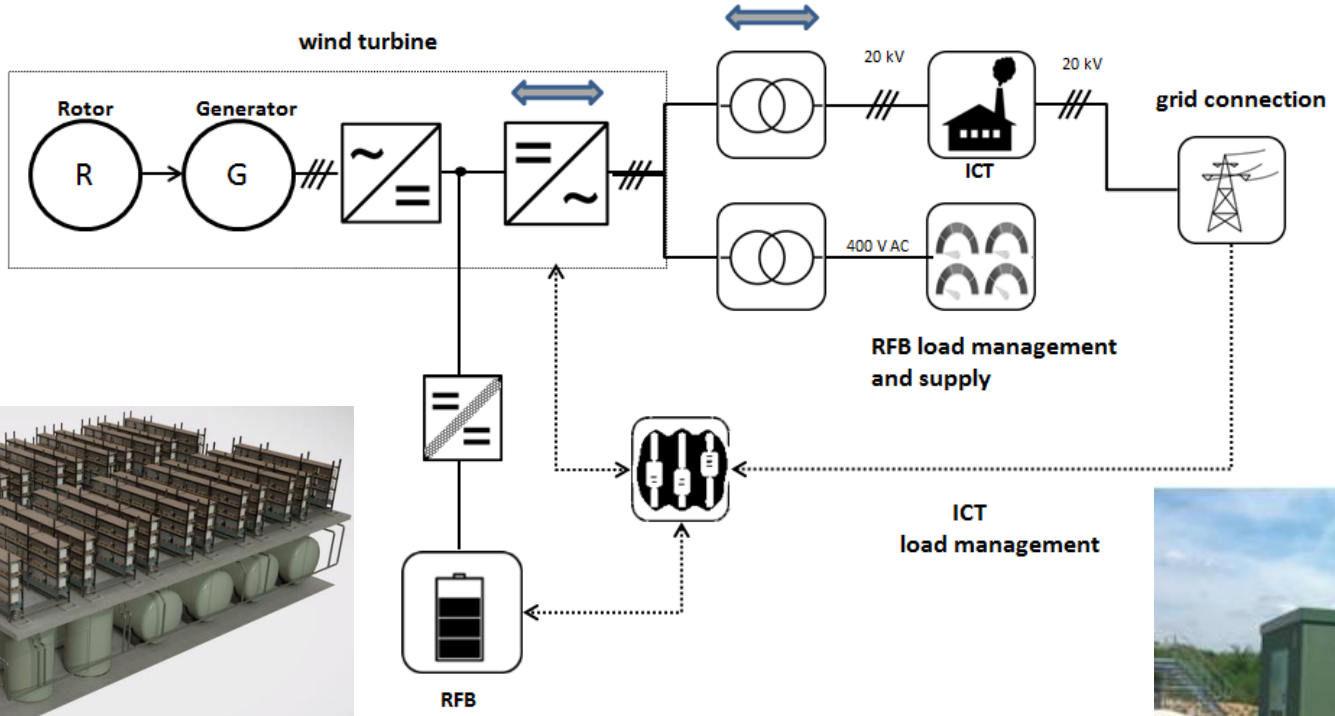
Funded by the county of Baden Württemberg

Bundesministerium für Bildung und Forschung

2MW wind turbine



2MW/20MWh VRFB



200 kW/200kWh LiFePo Battery

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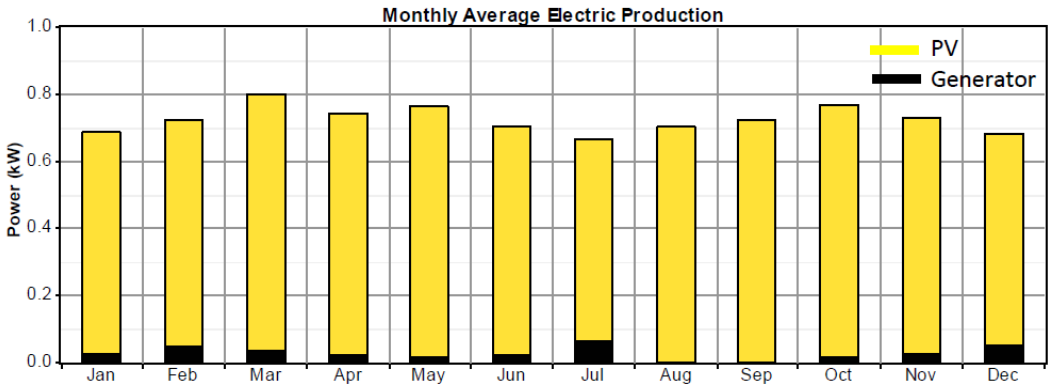
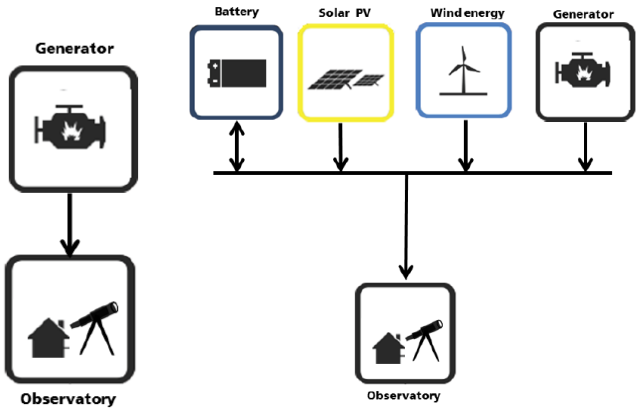
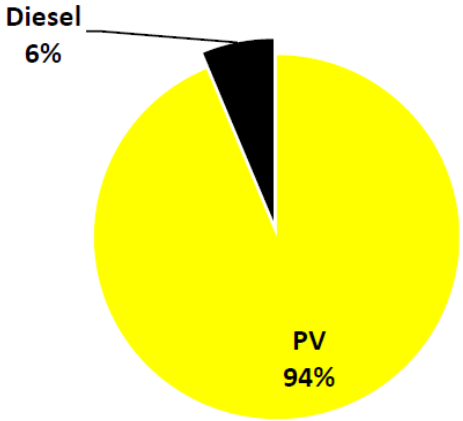
2012 - Ongoing - Standardisation of Flow Batteries

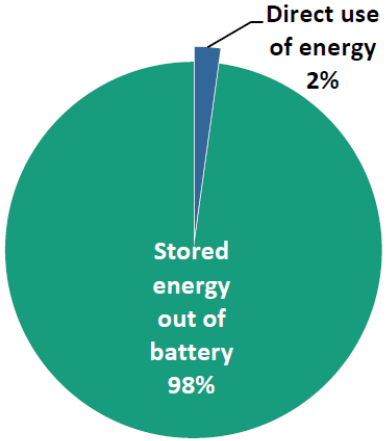
- **CENELEC European Committee for Electrotechnical Standardization**
  - CWA 50611: Flow batteries – Guidance on the specification, installation and operation, April 2013
- **International Electrotechnical Commission (IEC)**
  - **TC 21 JWG 82 „Secondary cells and batteries for renewable energy storage“**
    - IEC 61427-2: Secondary cells and batteries for renewable energy storage – General requirements and methods of test – Part 2: On-grid applications
  - **TC 21 JWG 7 „Flow battery systems for stationary applications“**
    - IEC 62932-1 ED1: *Flow Battery Systems for Stationary applications – Part 1: Terminology*
    - IEC 62932-2-1 ED1: Flow Battery Energy System for Stationary applications – Part 2-1: Performance general requirements and test methods
    - IEC 62932-2-2 ED1: Flow Battery Systems for Stationary applications – Part 2-2: Safety requirements
- **German National Committee**
  - DKE AK 371.0.6 „Flussbatterien“

2013 - Microgrid simulations

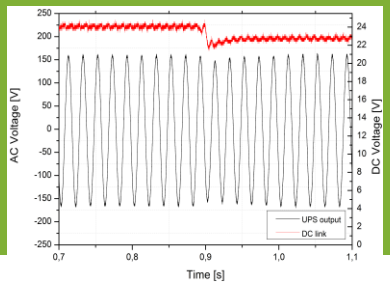


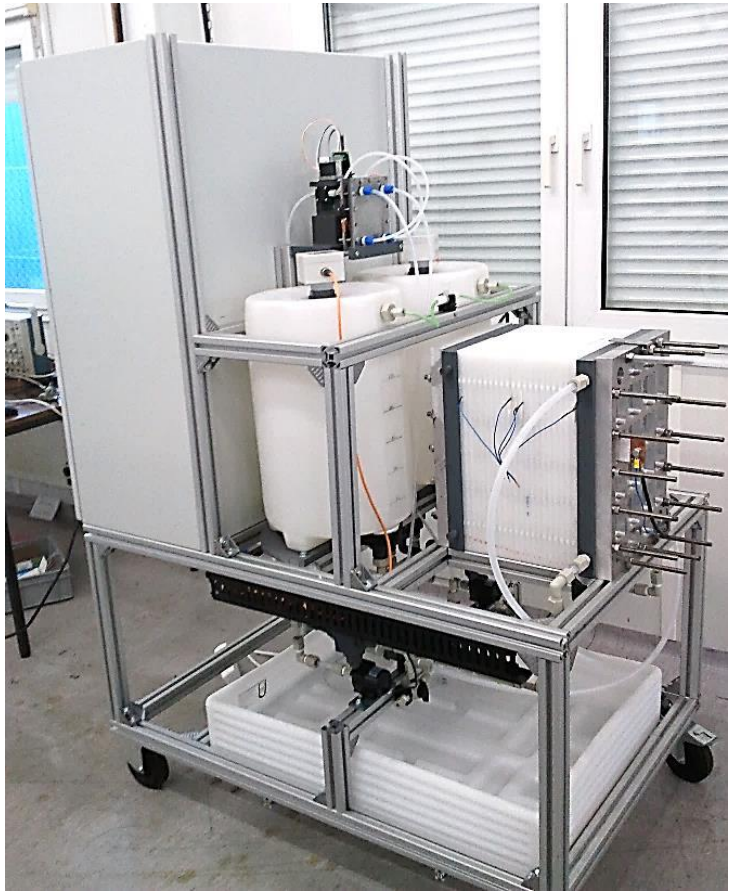






2014 - VFB uninterruptible power supply





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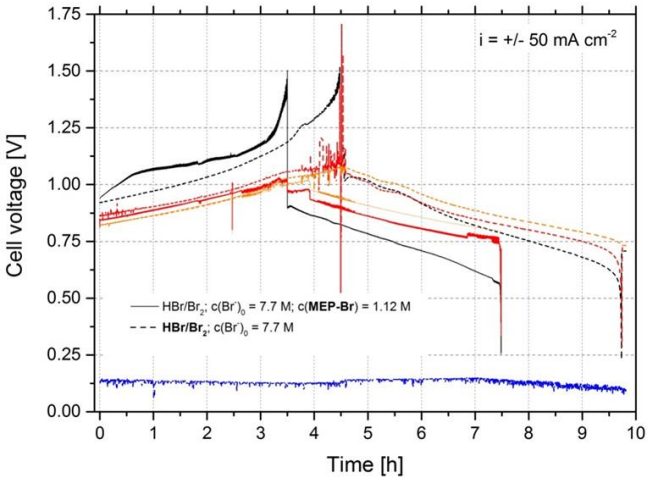
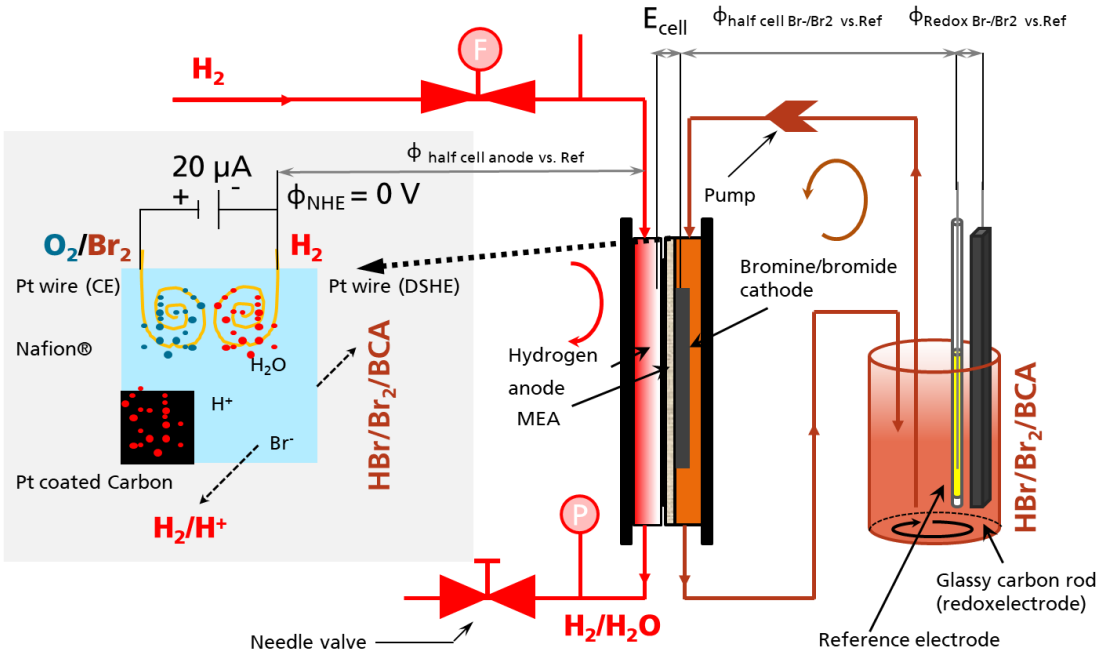
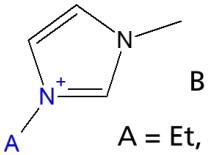
2014 - H/Br flow battery







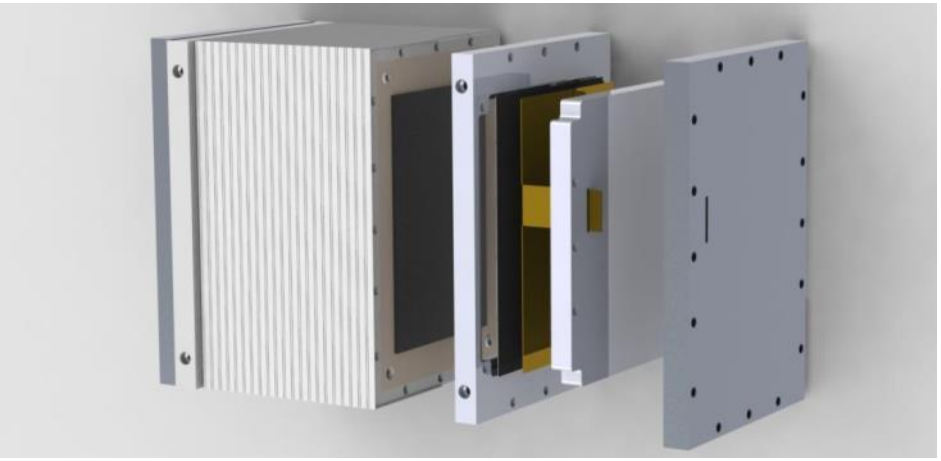
Imidazolium

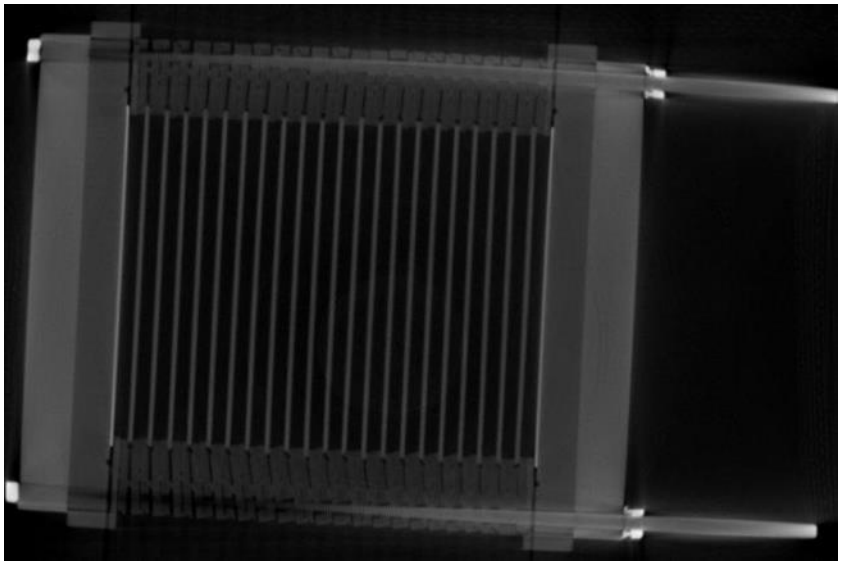
Bromid/Chloride

A = Et, Propyl, Butyl, Hexyl

- High current densities possibly, but
- complexing agents are blocking ion exchange membranes
- development of alternative complexing agents

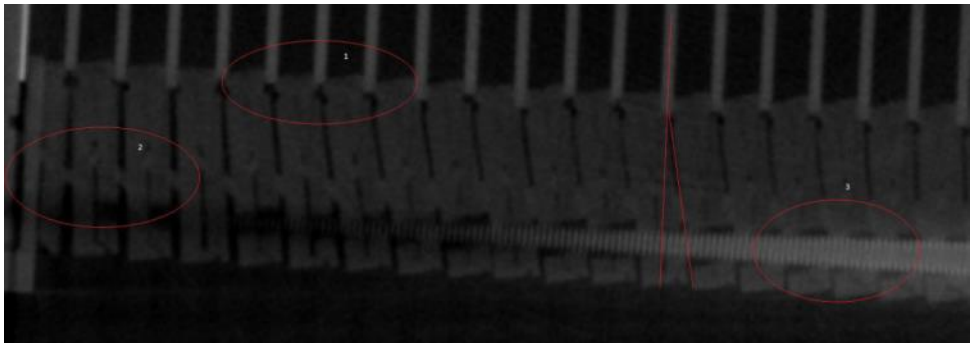
2015? - Computer Tomography of Stacks (1 kW class stack)





- **2D & 3D Measurements**
  - Construction Details
  - Any size !

- **Possibility for time resolved measurements**
  - Flow distribution in cells



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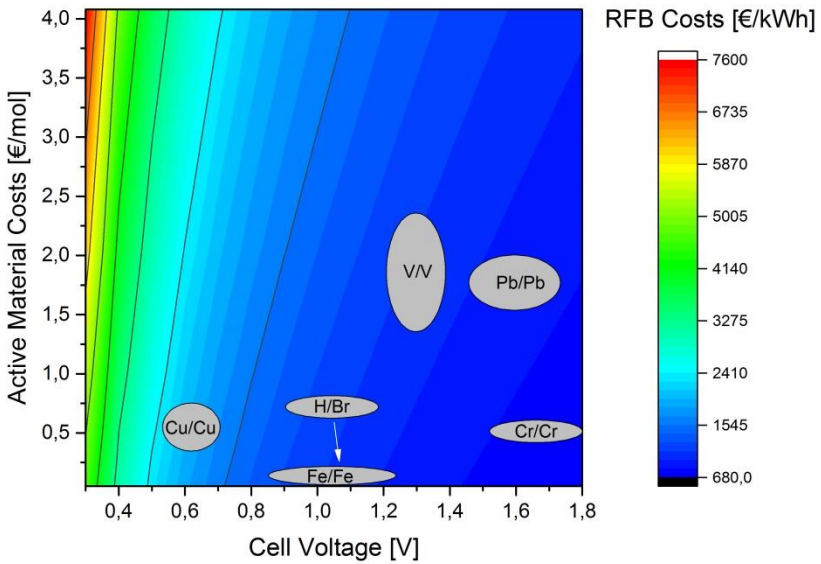
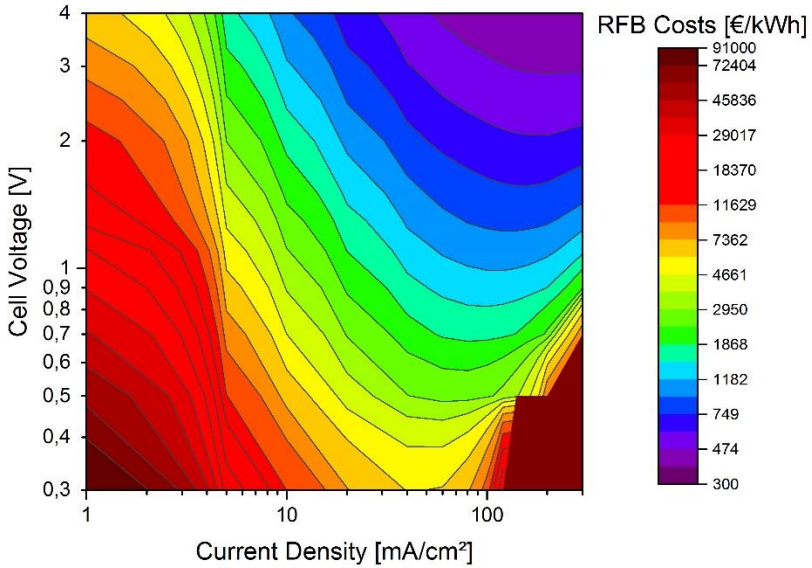
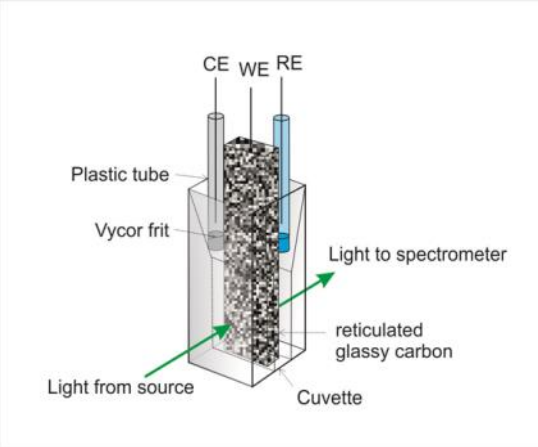
2016 - Techno-Economical Modeling and Simulation of Flow Batteries

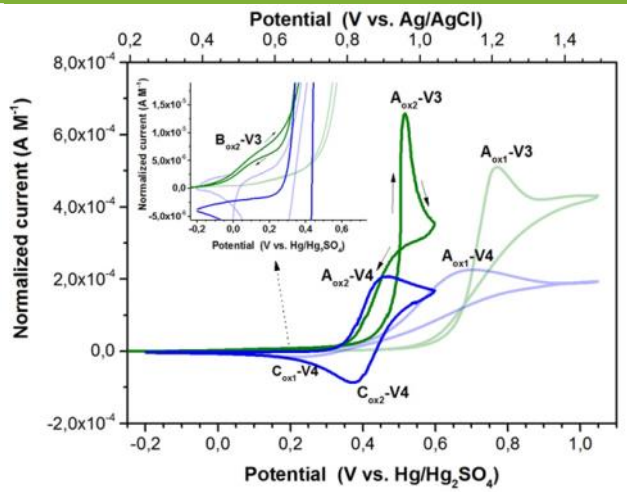


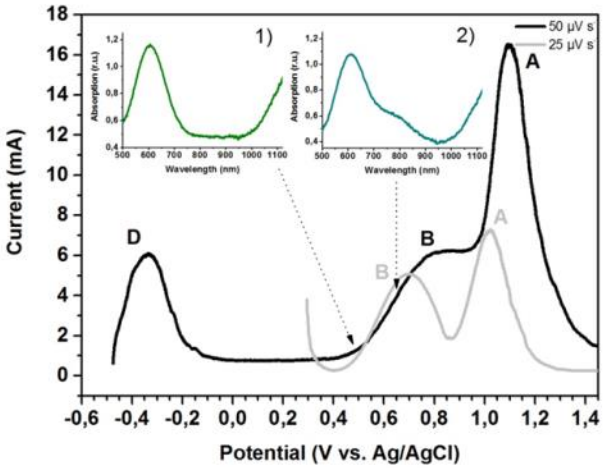


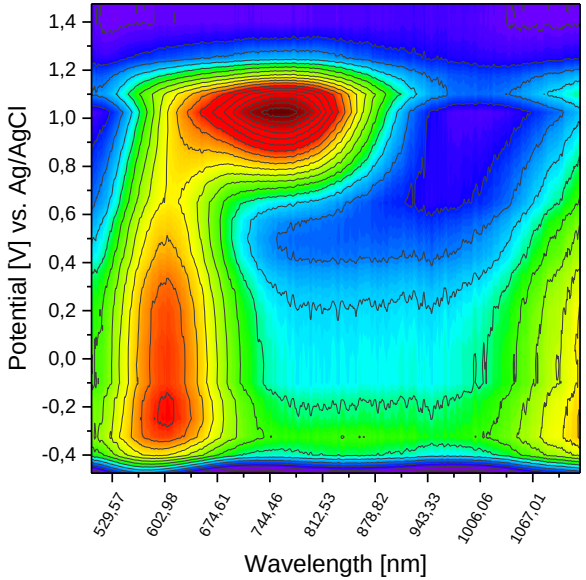
- Important Values for LCOE: CAPEX + Life time + Recycling
- Life time and recycling are currently the most important values compared to other technologies (LAB, LIB)
- **CAPEX ($/kWh) is not compareable!**

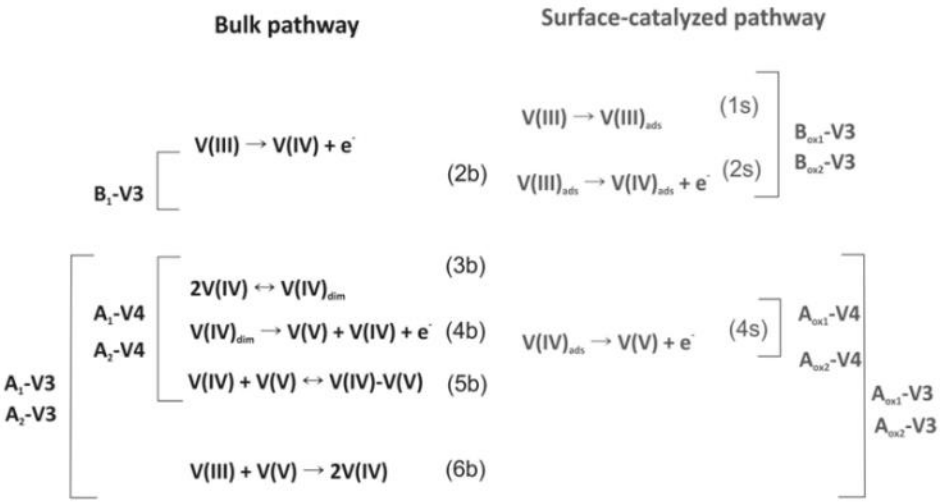
2016 - VFB – Oxidation Mechanisms of V(III)











N. Roznyatovskaya, J. Noack, M. Fühl, K. Pinkwart, J. Tübke, *Electrochimica Acta* **2016**, 211, 926–932.

VRFB – Upscaling to 2 MW/20 MWh

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VRFB – Upscaling to 2 MW/20 MWh

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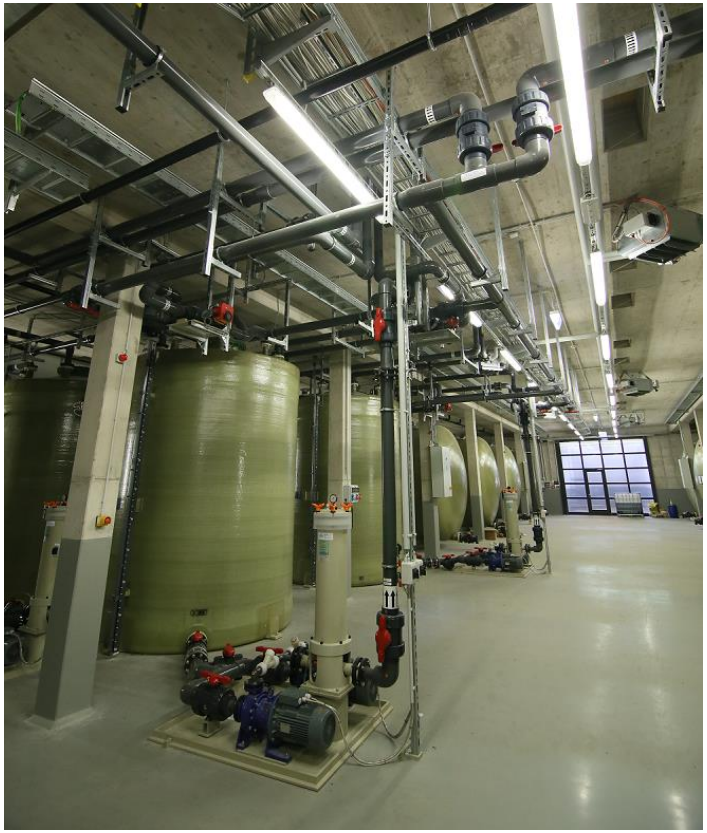
Bundesministerium für Bildung und Forschung



The first module has been put in operation end of December 2017.

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VRFB – Upscaling to 2 MW/20 MWh

Funded by the county of Baden Württemberg

Bundesministerium für Bildung und Forschung

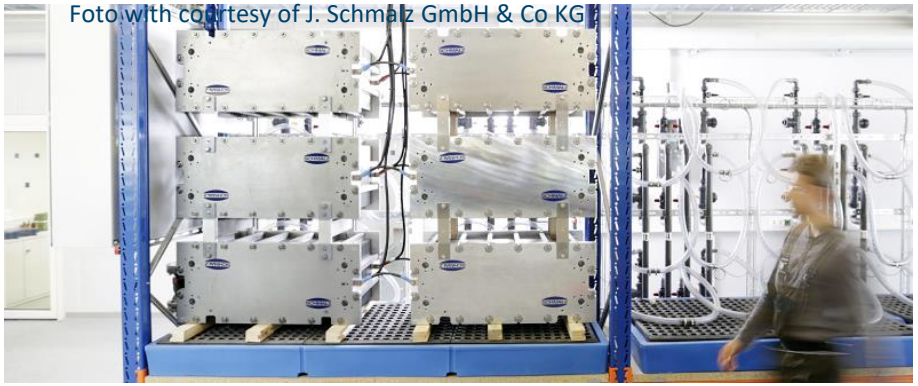

Foto with courtesy of J. Schmalz GmbH & Co KG

Current status:

- 42 Stacks are connected in the first half module and brought into operation. The first testing cycles confirms data measured on individual stacks
- Nearly 360 t (300 m³, 10 MWh) of the vanadium electrolyte has been filled in the tanks already.
- Wind turbine is in operation, but DC connection to battery will be established in 2018

Trumpf-Hüttinger DC-Power Electrinics für VRFB

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2017 - CENELEST

- **German-Australian Alliance for Electrochemical Technologies for Storage of Renewable Energy**
  - Project to establish a center (CENELEST) at UNSW/Sydney
  - Project start 08/2017, Collaboration Fraunhofer ICT - UNSW

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2017 - CENELEST

- Thematic focus is flow batteries but also liquid metal batteries and hydrogen
- UNSW developed the Vanadium Redox Flow Battery in early 1980s till today
- Fraunhofer ICT is developing many different Redox Flow Batteries since 2007 and installed Europe‘s largest Vanadium Redox Flow Batterie (2 MW/ 20 MWh)

--> Bringing together Fraunhofer applied research and UNSW basic research

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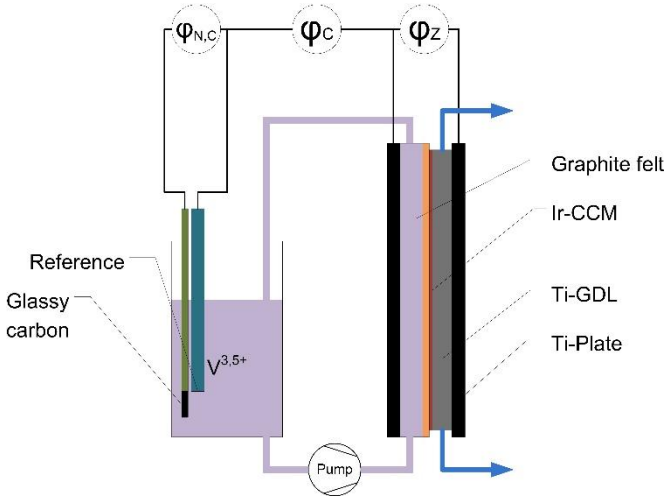
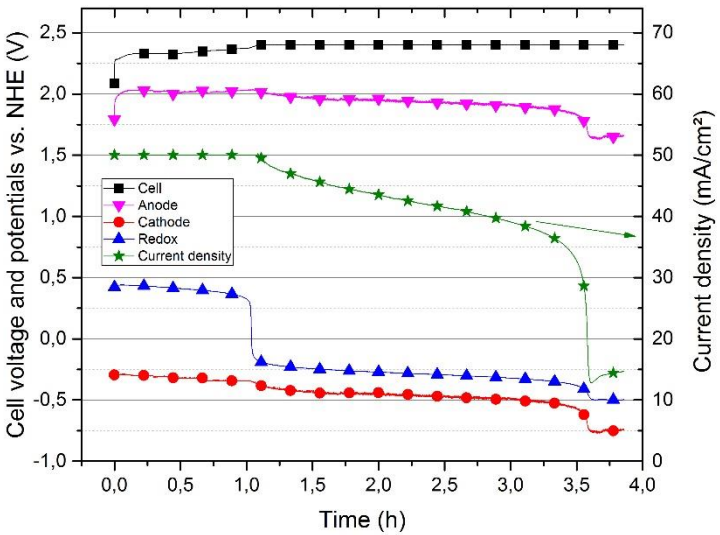
2017 - Vanadium/Water electrolyser – Recharge VOFC





$V^{3+} + e^- \rightarrow V^{2+}$ E $\varphi^0 = -0.255$ V

$VO^{2+} + e^- \not\rightarrow V^{3+}$ E $\varphi^0 = +0.35$ V

$VO^{2+} + e^- \rightarrow V^{2+}$ E $\varphi^0 = ?$

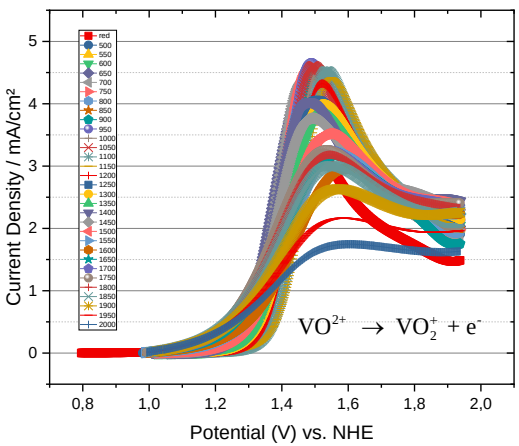
$V^{2+} + VO^{2+} \rightarrow V^{3+}$ C

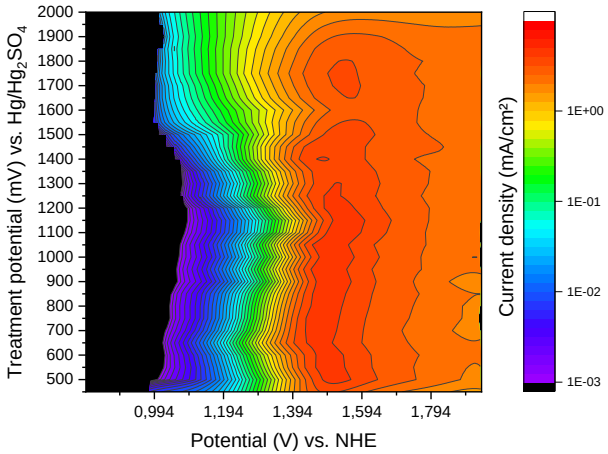
$V^{3+} + e^- \rightarrow V^{2+}$ E $\varphi^0 = -0.255$ V

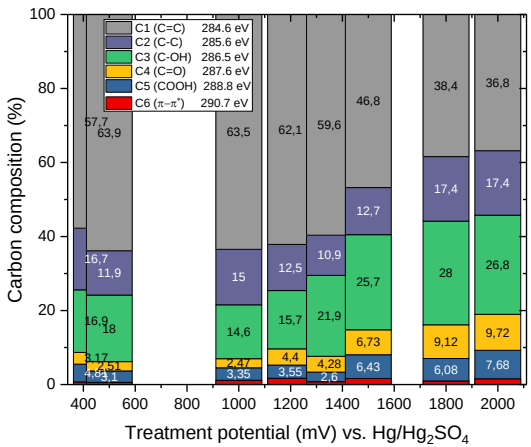
	$V^{3.5+}$ to V^{3+}	V^{3+} to V^{2+}
Theor. capacity (Ah)	2.06	4.12
Theor. energy (Wh)	1.63 (790 mV)[1]	6.26 (1.52 V)[1]
Capacity (Ah)	2.06	4.28
Energy (Wh)	4.99	10.27
Efficiency EE	32.7	61.0
Efficiency CE	100	96.3
Efficiency VE	32.7	63.3

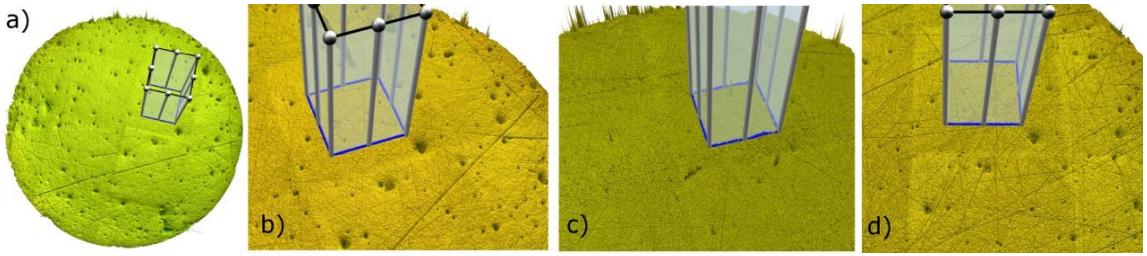
J. Noack et al., „Vanadium Proton Exchange Membrane Water Electrolyser“, Journal of Power Sources 2017, 349C, 144-151

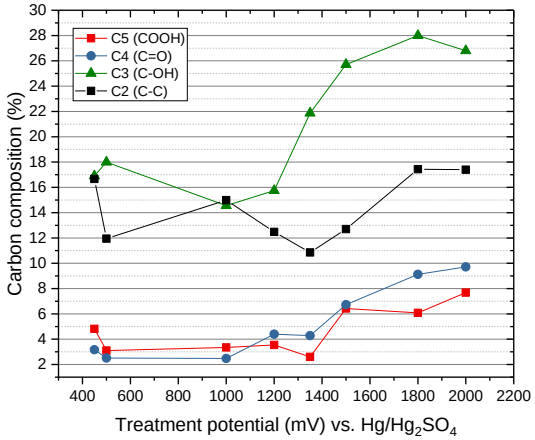
2018 - Electrochemical Pre-treatment of Electrodes for Vanadium Redox Flow Batteries







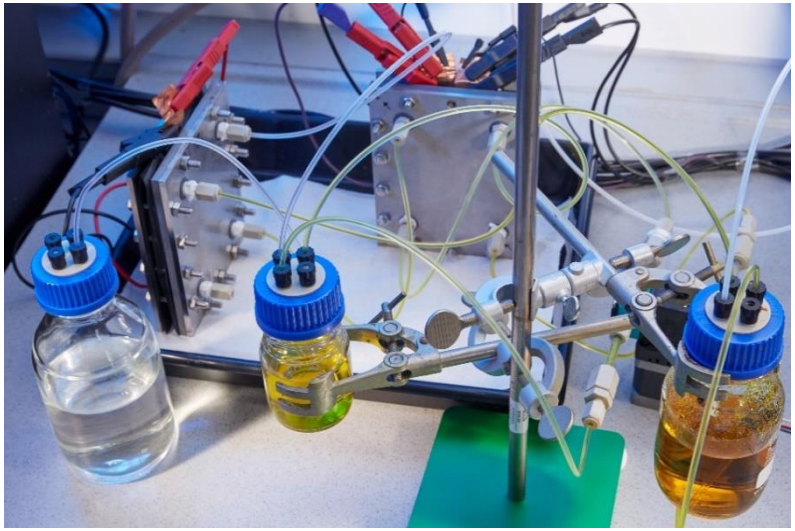


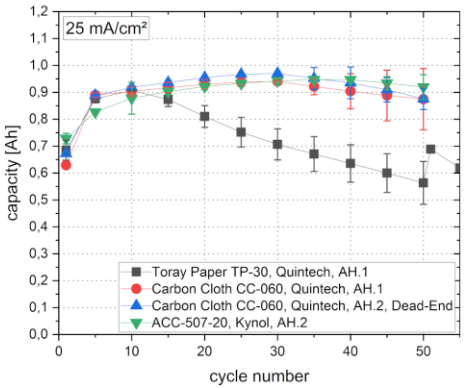


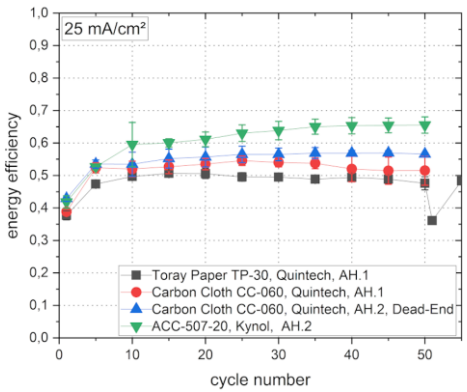
-> No correlation with surface roughness but weak correlation with functional groups – -C-OH for VO^{2+}/VO_2^+, -COOH for V^{2+}/V^{3+}

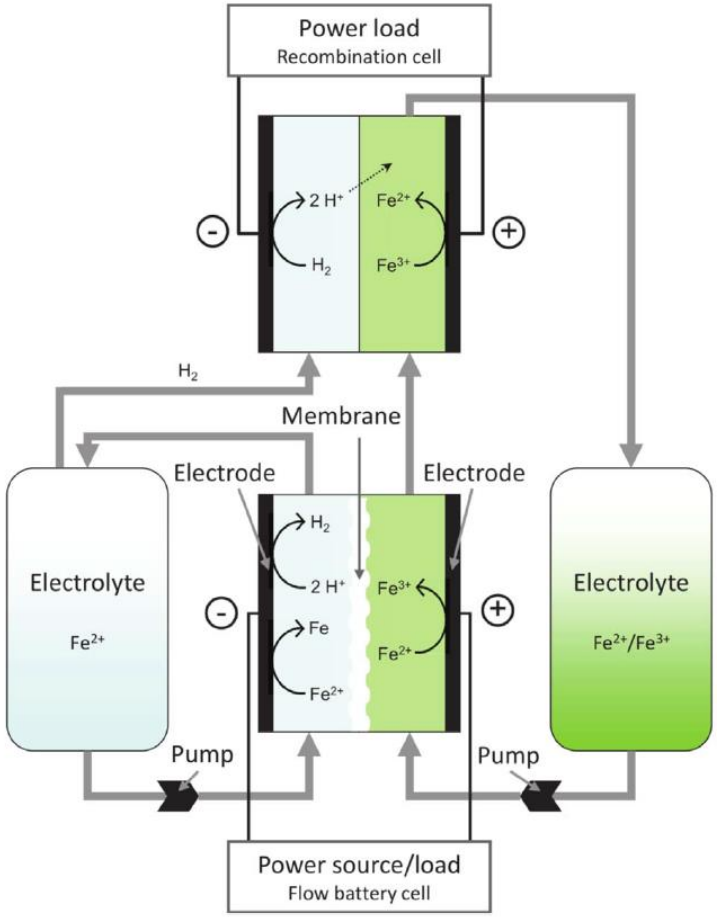
J. Noack et al., Journal of Energy Chemistry 2018, 27, 1341-1352

2018 (Ongoing) - Fe/Fe flow batteries

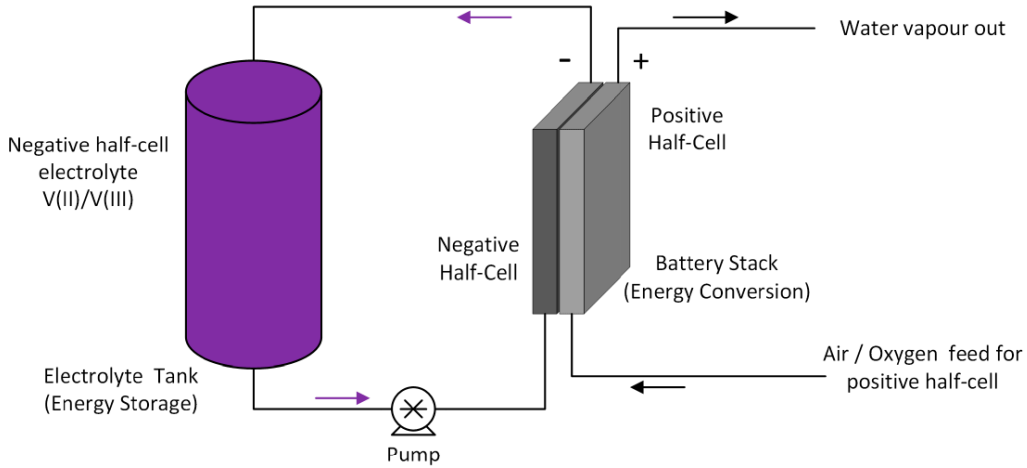


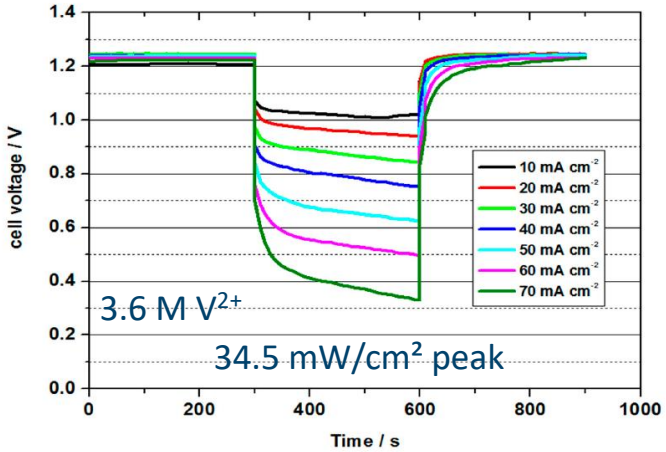


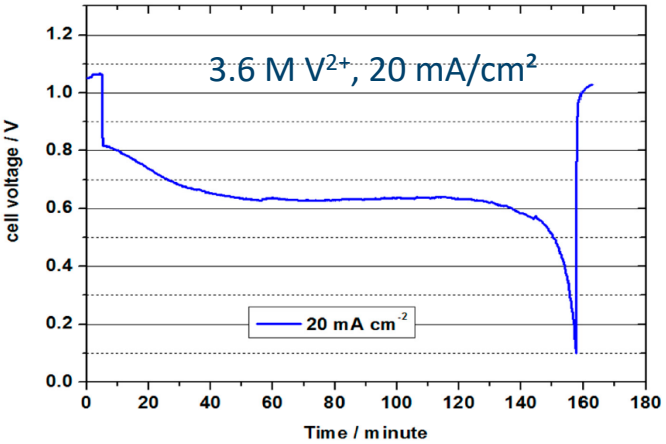




2019 - Vanadium Oxygen Fuel Cell (VOFC) – Gen 4 VRFB @ UNSW !







Anode: $V^{2+} \rightarrow V^{3+} + e^-$ $\varphi^0 = -0.255$ V

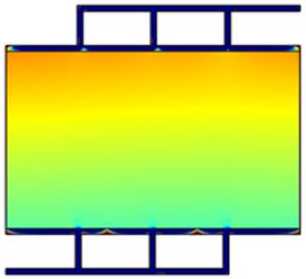
Cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ $\varphi^0 = +1.23$ V

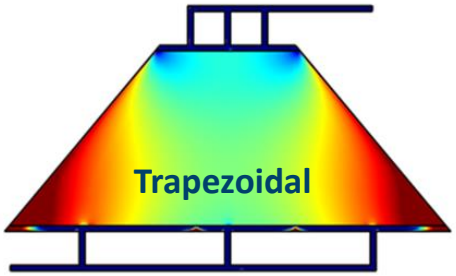
Cell: $4\,V^{2+} + O_2 + 4H^+ \rightarrow 4V^{3+} + 2H_2O$ $U_{cell} = 1.49$ V

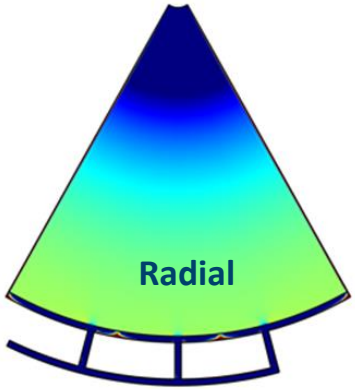
--> High theoretical energy density (3.6 M V^{2+} -> 143.8 Wh/L

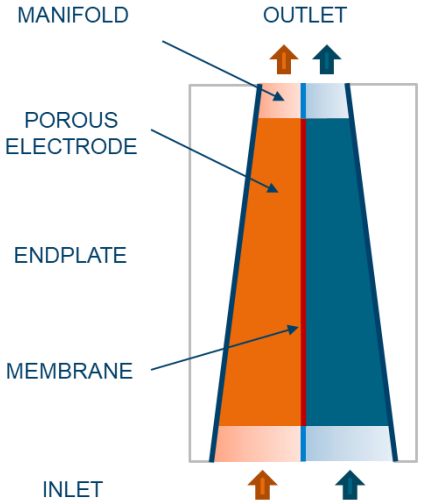
M. Risbud et al., „Vanadium Oxygen Fuel Cell Utilising High Concentration Electrolyte“, Batteries 2019, 5(1), 24

2019 - Stack and Cell Concepts for Redox Flow Batteries @ UNSW !

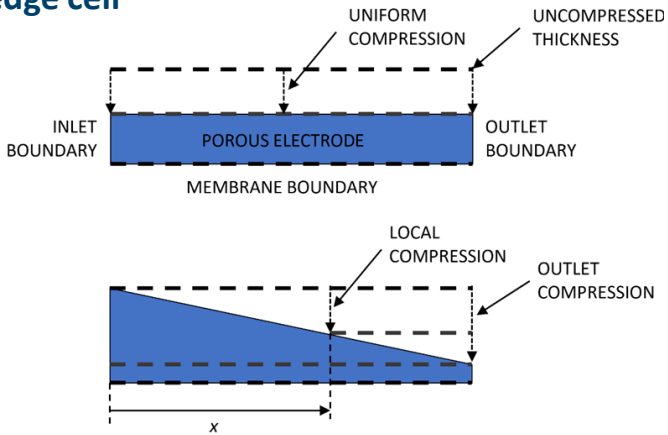




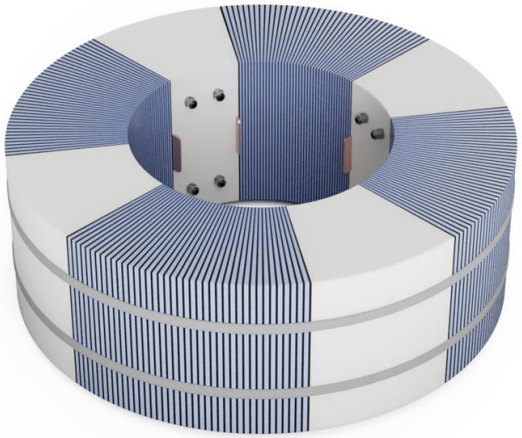




Wedge cell



Wedge cell – Toroidal stack



N. Gurieff et al. Appl. Sci. 2020, 10(8), 2801; N. Gurieff et al., Batteries 2018, 4(4), 53; N. Gurieff et al., Molecules 2019, 24(21), 3877

2019 - Flow Batteries for Maritime Applications

- **Zero-emission shipping - Electrification of maritime vessels**
- Recharging of the Vanadium Redox Flow Battery by fluid exchange

- 500 miles, 15 knots, 30 hours, 240 MWh, 8 MW
- ~ 5000 m³ electrolyte

VANADIUMCORP
CLEAN ENERGY SOLUTIONS

CONOSHIP INTERNATIONAL
MARITIME INNOVATION AWARD WINNER 2019

ENELEST
German-Australian Alliance for Electrochemical Technologies for Storage of Renewable Energy

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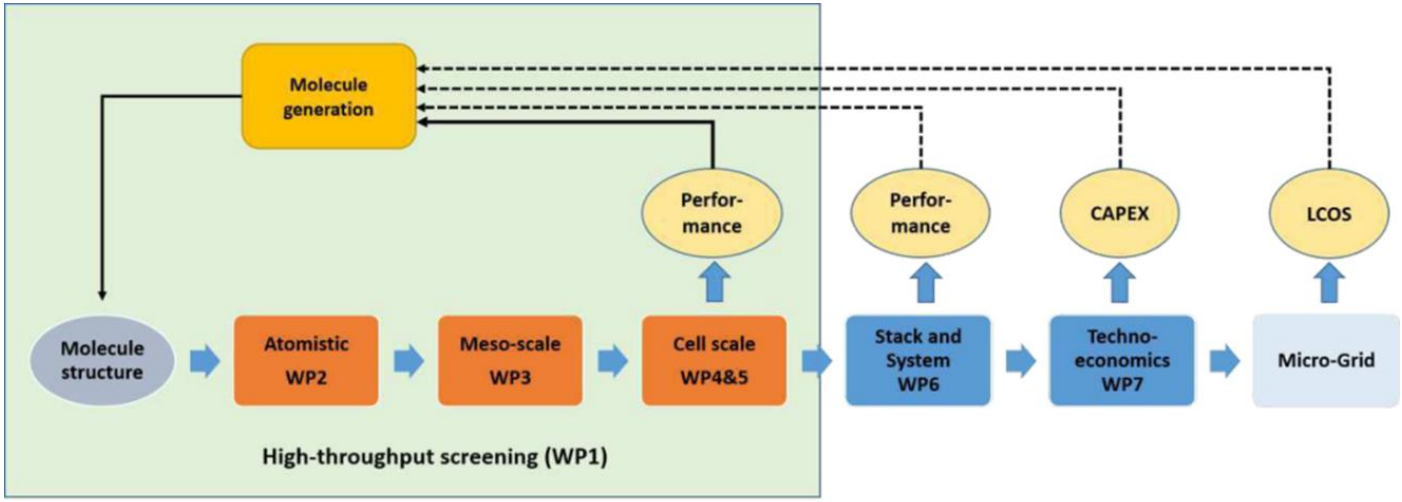
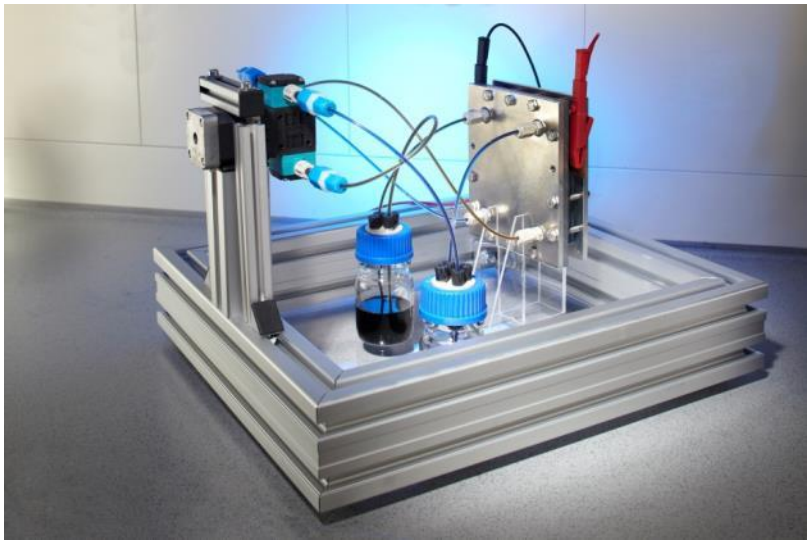
2020 - Modelling for the search for new active materials for flow batteries (SONAR)

H2020-LC-BAT-2019-2020 (LC-BAT-3-2019)
Project start: January 2020
Project end: December 2023 (4 Years)

Partner: 7 Institutions, 4 Universities, 2 Research Organisations, 6 Companies (IEB)
Coordinator: Fraunhofer Gesellschaft (Germany), Jens Noack + Carolyn Fisher
5 Countries, 3 EU Countries, 1 H2020 Associated country (Switzerland), 1 External (Australia)
Project funding: 2.8 M€ 2.4 M€ (EU), 430 k€ (UNSW Australia)



Thank you for your attention!



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