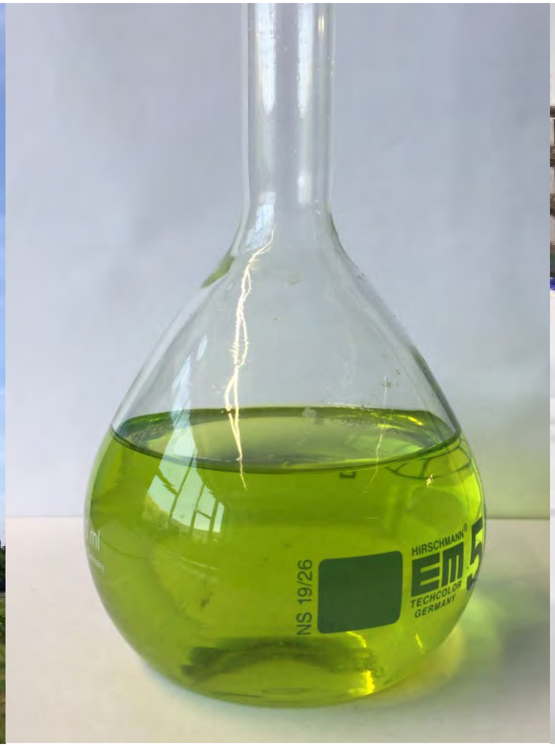
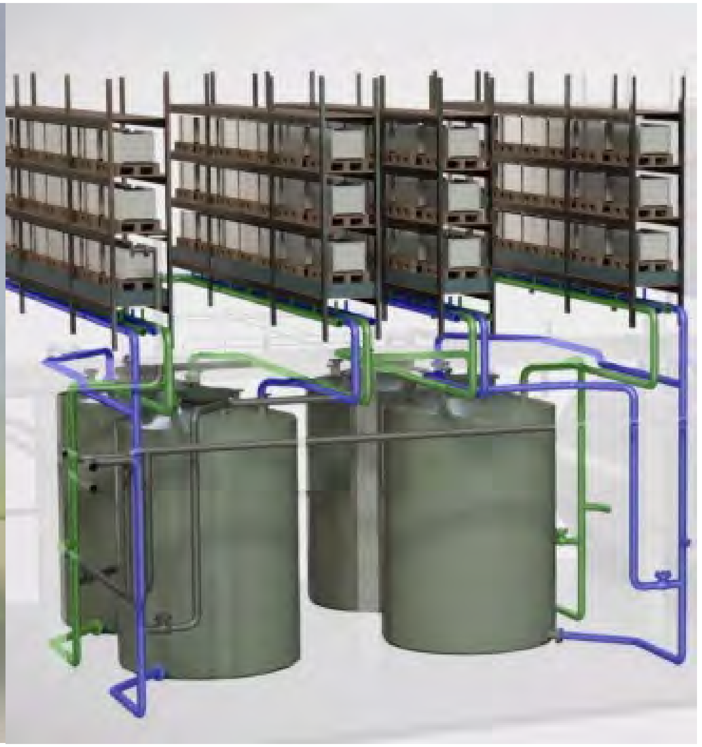
REDOX FLOW BATTERIES – FROM RESEARCH TO APPLICATION

Dr. Peter Fischer

HIGREEW Workshop, Pilsen 2. Feb. 2022



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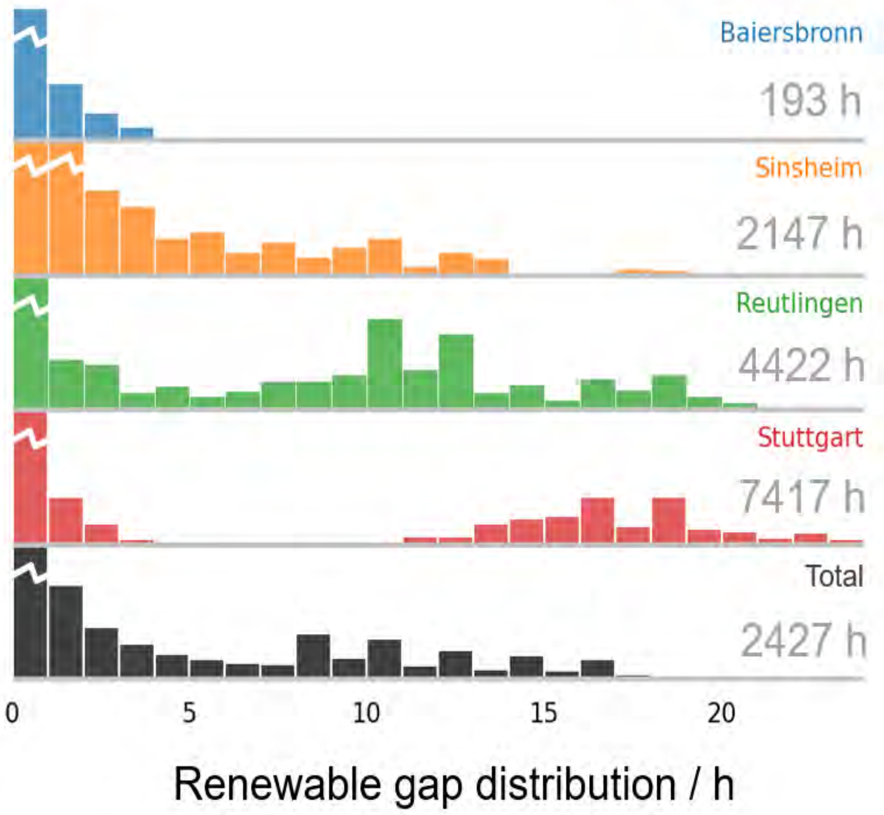
Motivation



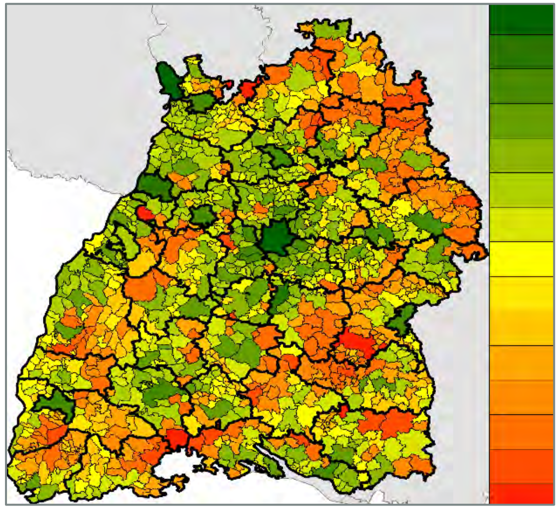
In Fraunhofer Project StiL Fraunhofer ICT modelled the storage demand of the county of Baden-Württemberg for 90-100% of renewable energy utilization (goal by 2050).

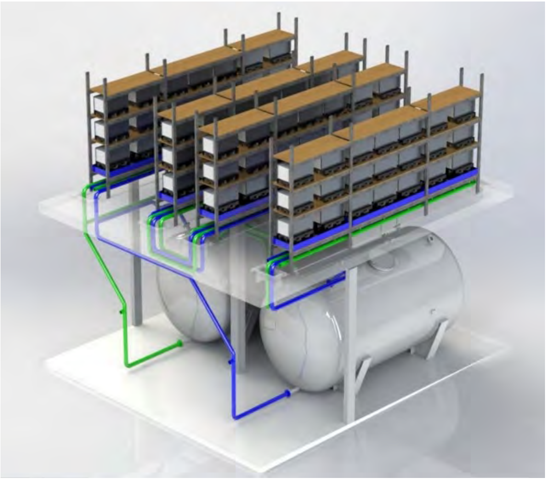
One prelimenary result is the storage gap in different areas of the county.

For areas with potentially high wind& solar utlization, the renewable energy gap can be a few hours.

For areas with potentially low wind utilization, renewable energy gaps another maximum between 8-10 hours appear.

This gap can be closed in dayly operation with long-duration storage.





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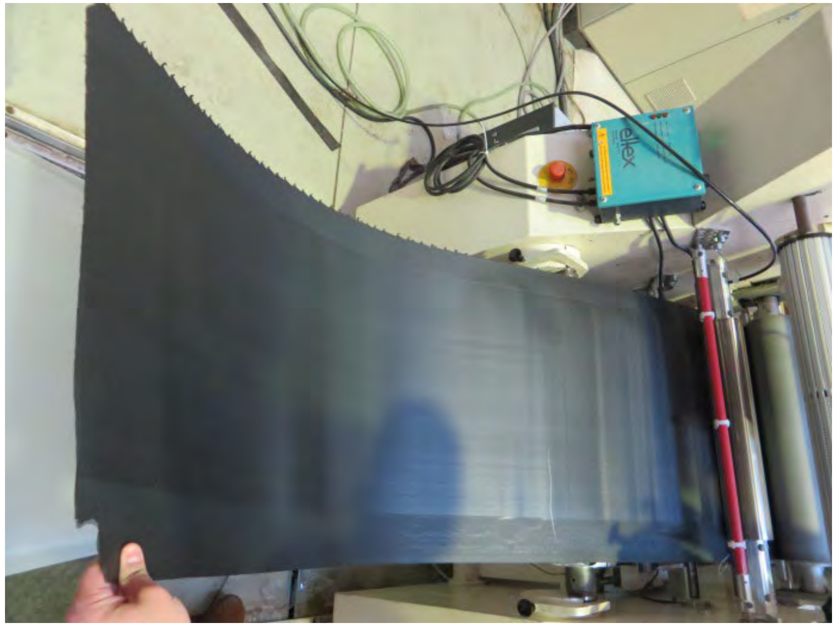
Applications

Two use cases act as an example how Fraunhofer ICT upscaled a laboratory process to bring the costs down.

Recycling of spent Vanadium electrolytes



Graphite based bipolar plate

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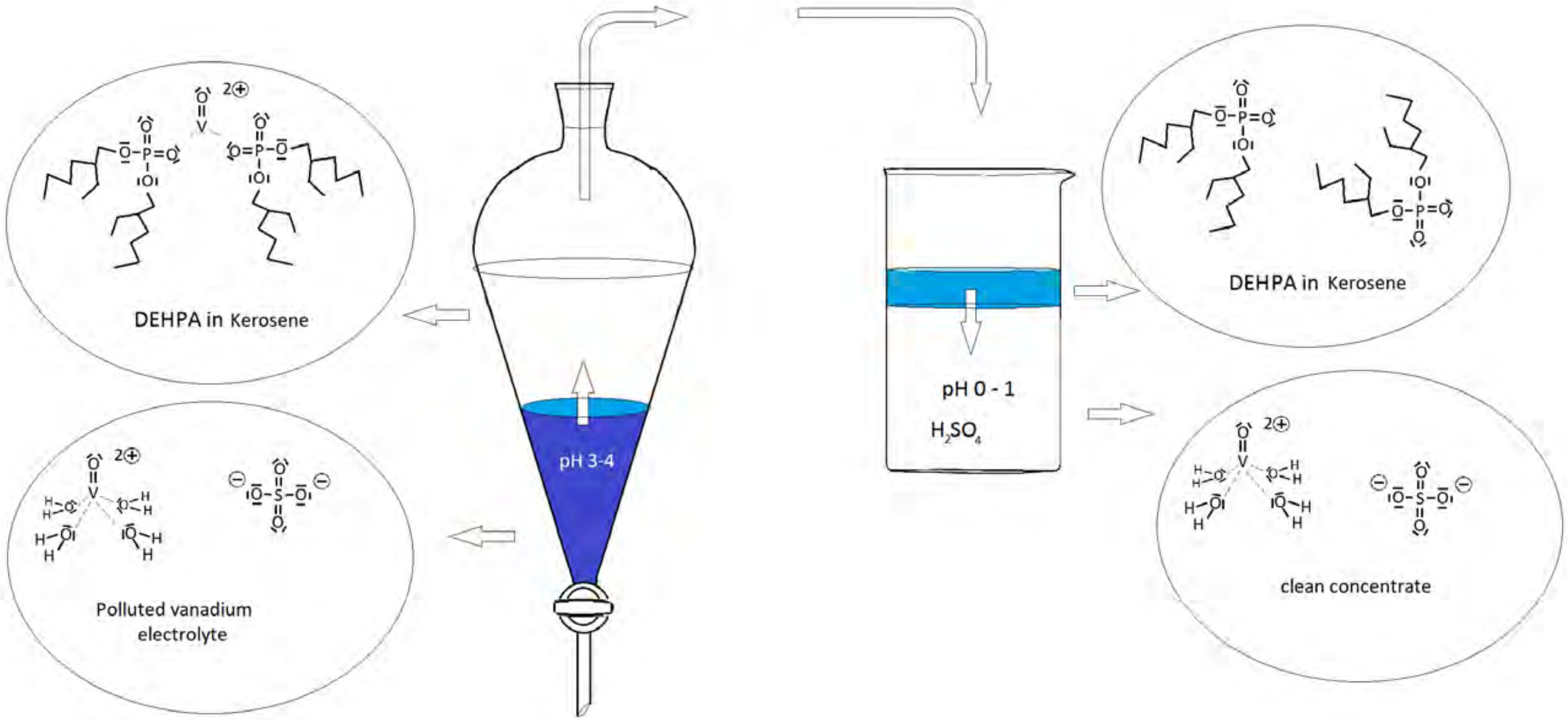
Recycling of vanadium electrolytes

Dr. Peter Fischer, Michael Schäffer



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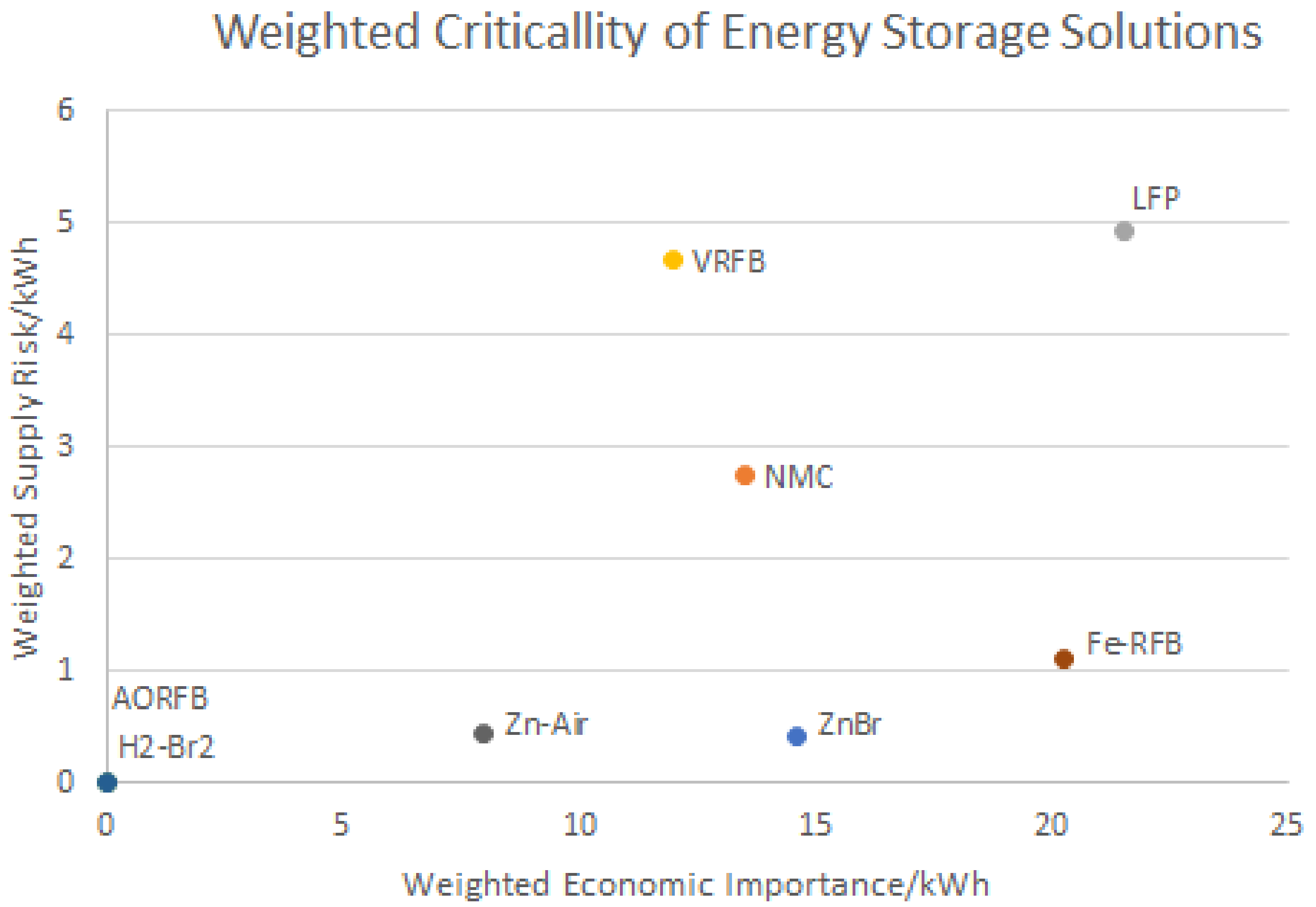
Motivation - Criticality of batteries



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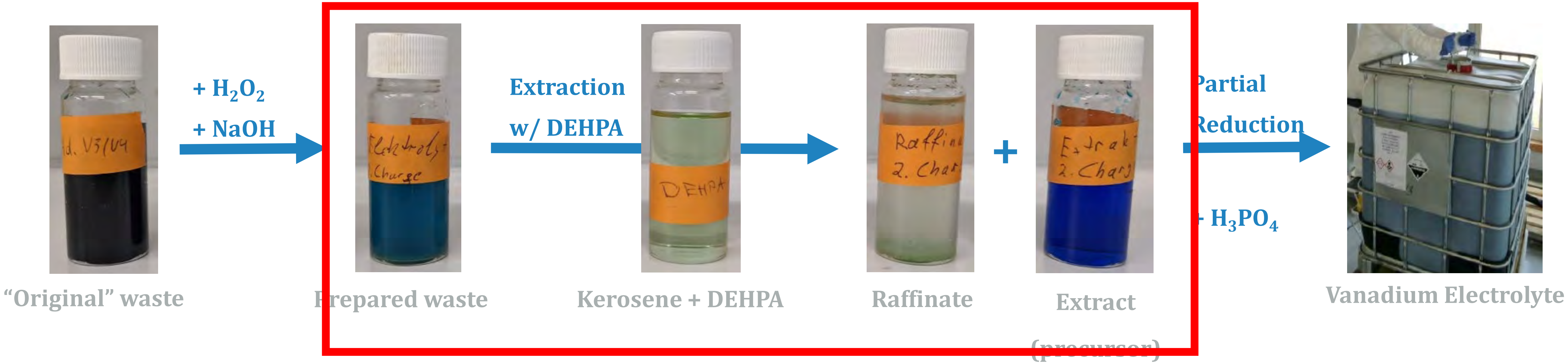
Recycling – complete process

- Complete Recycling process: 3 steps
  - Pre-processing: oxidation of waste solution to ~100% V^{4+}, setting of pH
  - Extraction: extraction of V^{4+} with DEHPA/kerosene
  - Post-processing: Reduction to V^{3+} / V^{4+} mixture, addition of additives



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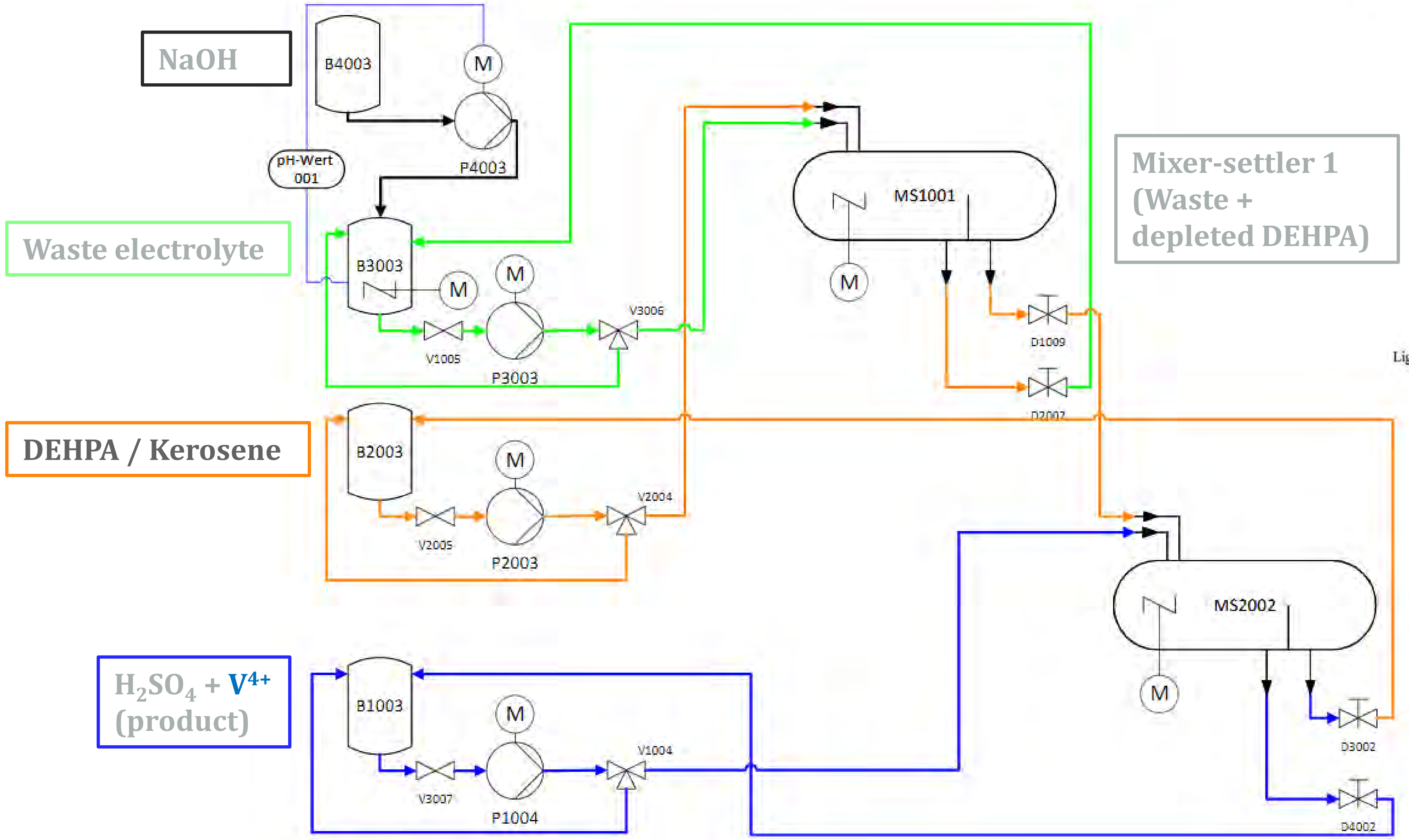
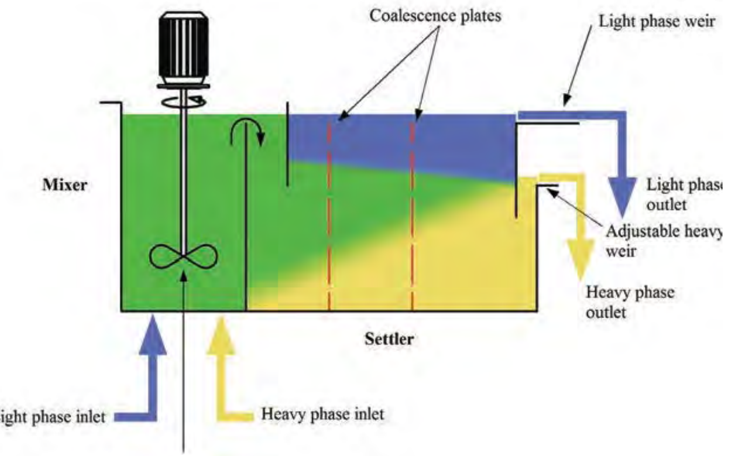
Extraction: recycling plant





https://en.wikipedia.org/wiki/Mixer-settler

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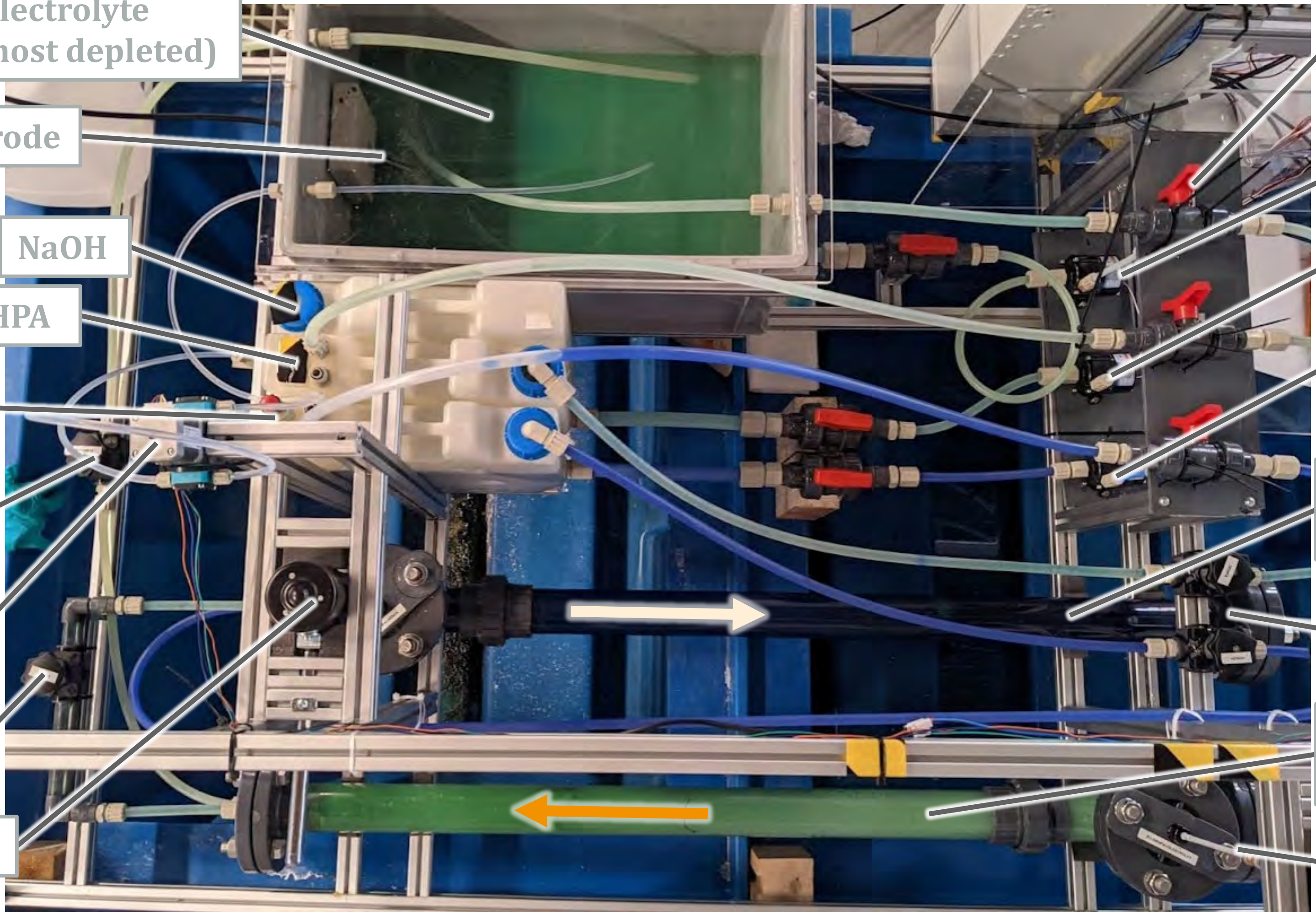
Extraction: recycling plant



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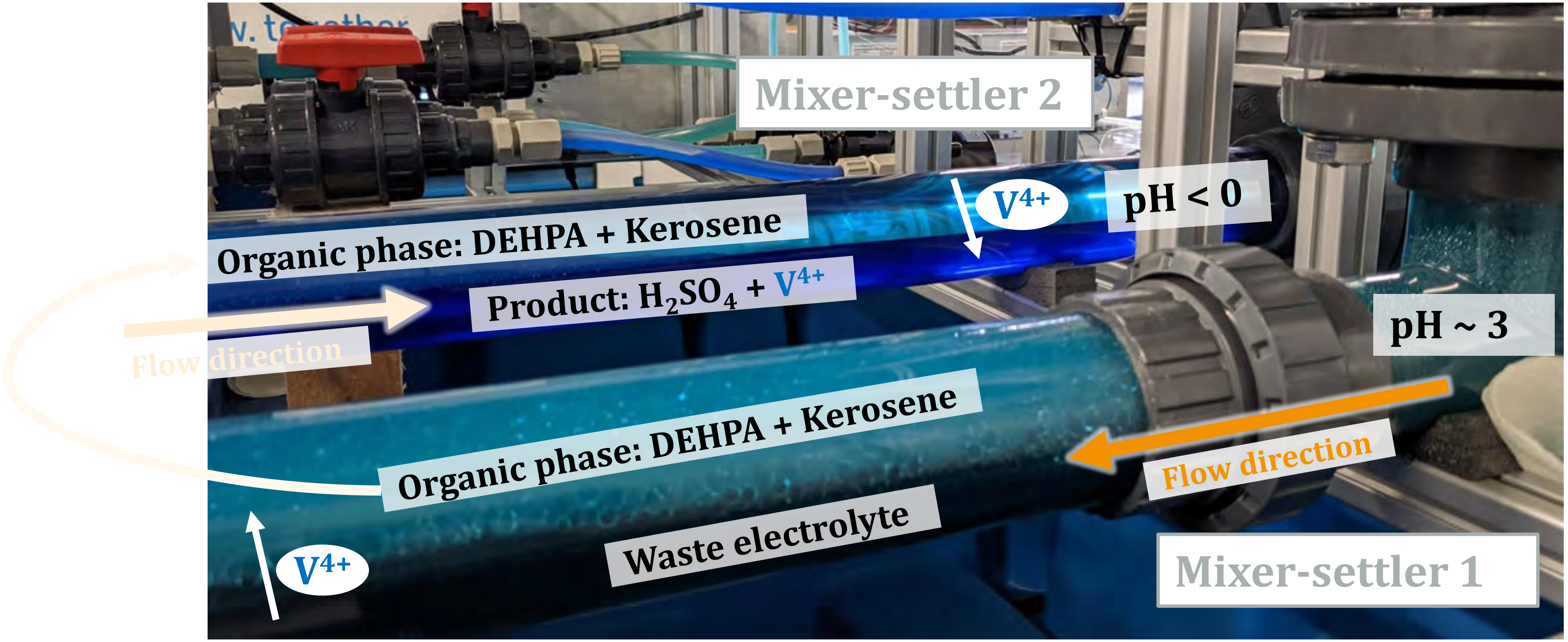
Extraction: recycling plant

- Extraction in continuous process using mixer-settlers



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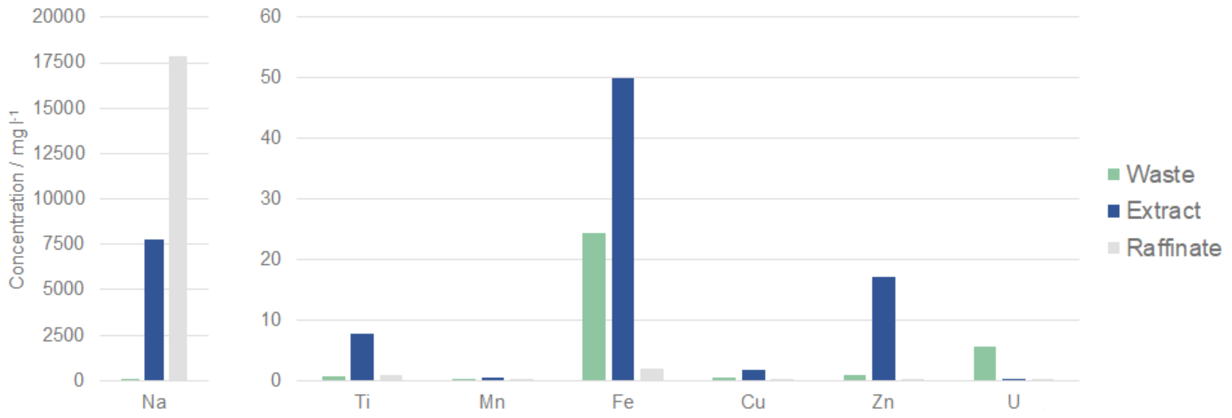
Results – Vanadium concentrations

- Original electrolyte sample → **“waste electrolyte”**
  - Molarity: 1.65 mol/l
  - Vanadium ratio (**V^{4+}** / **V^{3+}**): 52.7 / 47.3

Medium	Total V (mol/l)	V(III) (%)	V(IV) (%)
Waste solution	1.65	47.3	52.7
Pre-processed waste	0.33	3.3	96.7
Extract (precursor)	1.64	2.1	97.9
Raffinate (waste)	0.002	42	58
Product electrolyte	**1.75**	**49.3**	**50.7**

Enrichment of some elements

-> sodium



Increase in V concentration

→ presumably due to water cross-over, evaporation during electrolysis

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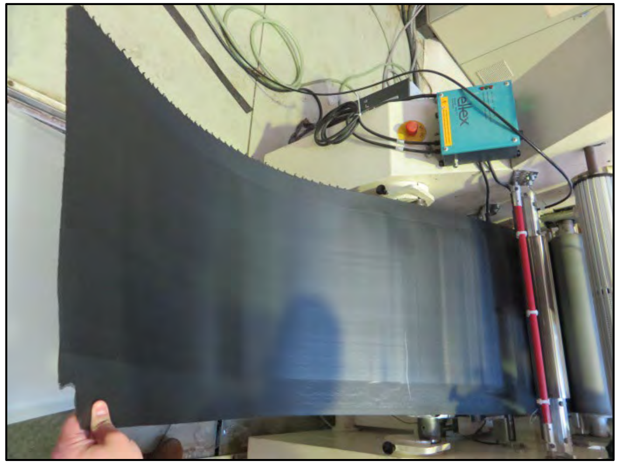
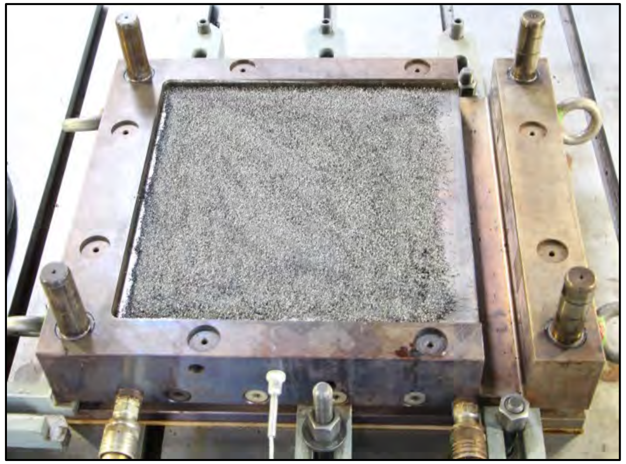
Next steps

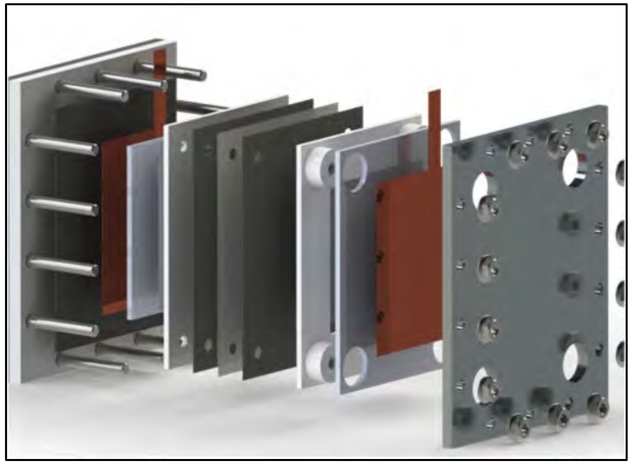
Next steps:

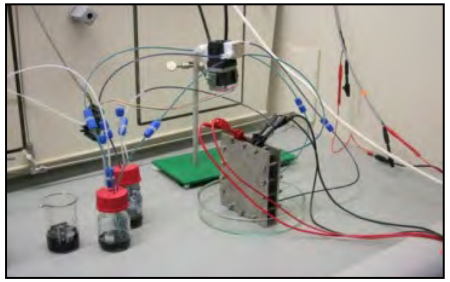
- Improve preparation of electrolyte (Oxidation process)
- Improve automation of recycling plant; so far manual adjustments on needle valves necessary to balance out the different flows → addition of flow sensors for precise flow control
- Start testing with “real” waste electrolyte
- Performance testing with recycled electrolyte solution
- Work on automation of pre- and post-processing steps

C-COMPOSITES FOR BIPOLARPLATES IN RFB STACKS

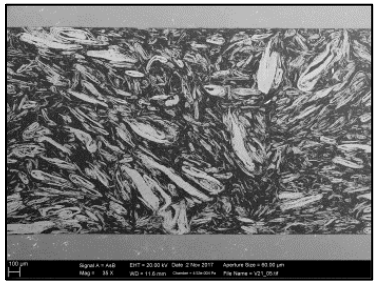
Dr. Peter Fischer, Dr. Christof Hübner



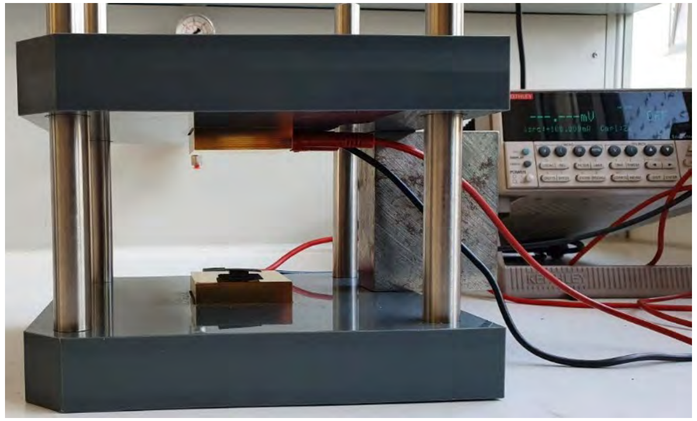




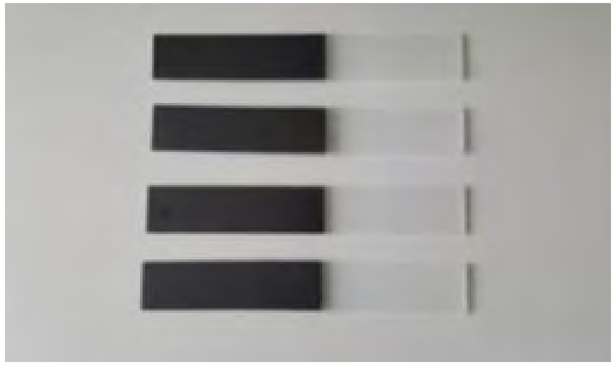



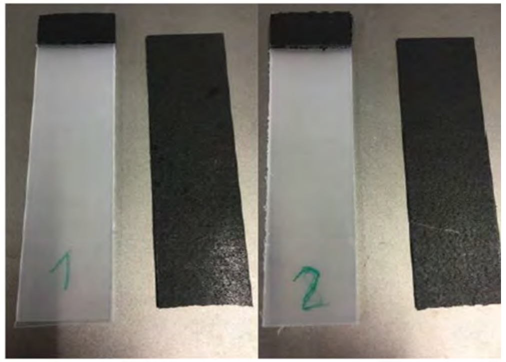
Targets for weldable bipoler plates

1. Fair electrical conductivity



2. Mechanical integrity of the welding seam





3. Chemical stability

DOE-targets (fuel cells) adapted to redox flow batteries

Parameter	Unit	DOE Targets
Plate Cost	$\$ * kW^{-1}$	5
Plate Weight	$Kg * kW^{-1}$	<0,4
Durability test (V^{2+}/V^{3+}+V^{4+}/V^{5+})	days	>840
Corrosion[1]	$\mu A * cm^{-2}$	<1
Resistance[2]	$Ohm * cm^2$	<0,02
Resistivity	Ohm*cm	<0,01
Flexural Strength	MPa	>25
Flexibility	%	3 – 5
Durability with cycling	h	10 000[3] (?)

[1]Electrolyte consist of 2M H_2SO_4 solution cycled between -0.3 V and + 1,3V (NHE) at 20 °C at slow scan rate (?)
[2]Resistance including the contact resistance at 140 N/cm^2
[3]<10% drop in power

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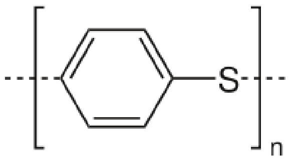
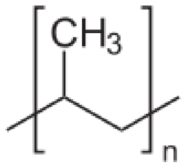
Graphite - CNT masterbatches for electr. conducting compounds

POLYMER MATRIX



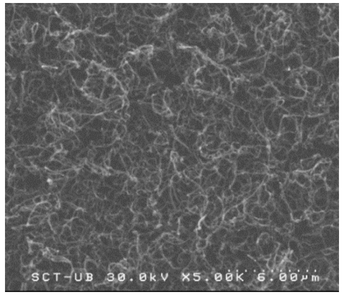
POLYPHENYLENE SULFIDE (PPS)



POLYPROPYLENE (PP)

CONDUCTIVE FILLERS

GRAPHITE



CARBON NANOTUBES

COMPRESSION MOLDING

INJECTION MOLDING

By addition of less than 2 wt.% CNTs into highly graphite filled matrix:

- 4 to 10 times increase in through-plane and bulk (in-plane) electrical conductivities of PPS and PP-based bipolar plates (BPP) respectively.
- 15 % improvement of Flexural Strength value for Injection Moulded PPS-based BPPs.

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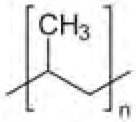
Graphite - CNT masterbatches for electr. conducting compounds

PP-BASED



Form: Granule

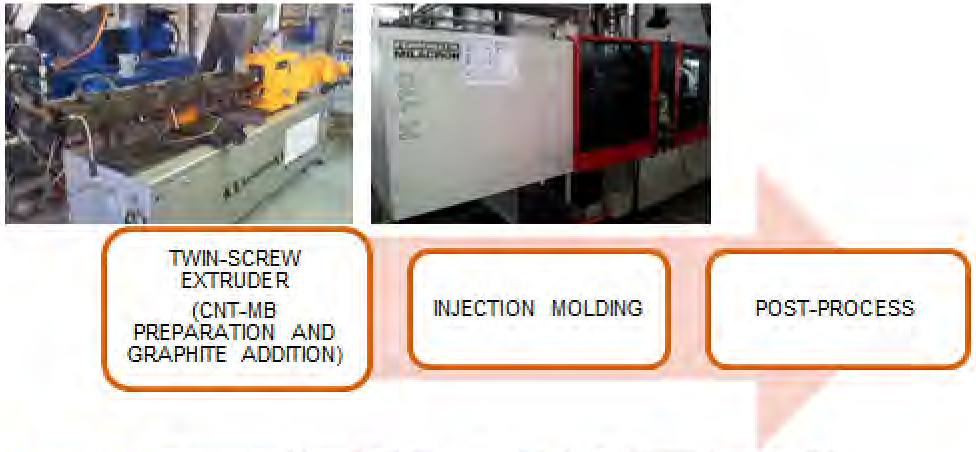
Homopolymer

Semi-crystalline

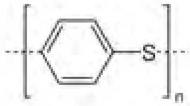
Melting temperature: 156-160 °C

Processing temperature: 210 °C

*Tensile Strength: ~30-35 MPa



PPS-BASED



Form: Powder

Semi-crystalline

Melting temperature: 280-290 °C

Processing temperature of 315 °C

*Flexural strength: ~50 MPa

*Tensile strength: ~35 MPa

*Similar grade

First recipies concentrated on injection molding:

- Process parameter were optimized to be used in conventional injection molding machines
- The compound is cost optimized for costs of below 10€/kg compound

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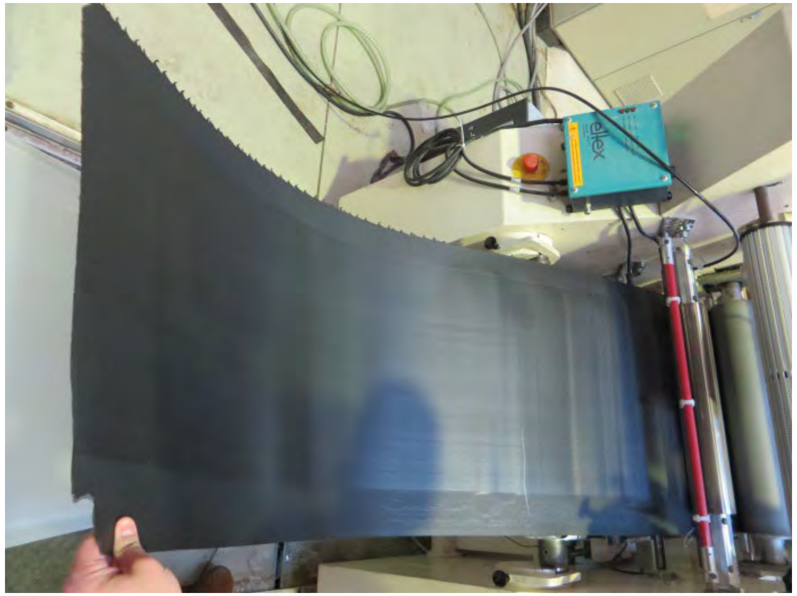
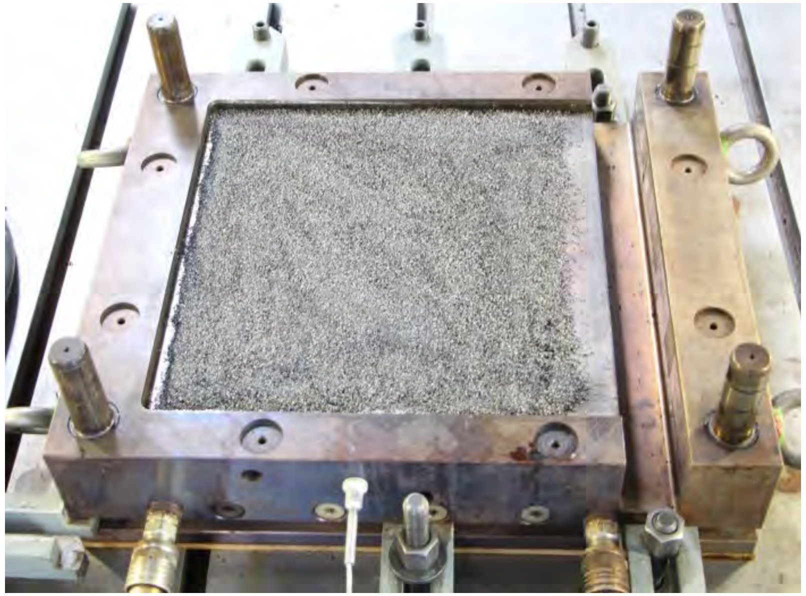
Graphite - CNT masterbatches for electr. conducting compounds

The newest version of C-Compounds for RFB are based on PP. They can be processed with…

- Hot-Pressing
- Conventional Injection molding machines
- Endless extrusion (up to 60% carbon filling possible)





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Graphite - CNT masterbatches for electr. conducting compounds

Bipolar Plates	In-plane El. Conductivity (S/cm)	Through-plane El. Conductivity (S/cm)	Thickness (mm)	Advantages	Disadvantages
Schunk FU 4369*	110,0	52,6	3,0	• High electrical conductivity	• High costs • No welding • Low processability
Eisenhuth PPG-86*	55,0	18,0	3,0	• High electrical conductivity	• High tolerance (thickness) • No welding • Low Processability
Extruded BPP (ICT) 55 wt.% Filler	10,0 – 15,0	0,9 – 1,2	0,7 – 1,4	• Low carbon loading • Cheap graphite filler • Low cost • Processability • Welding possible	• Relatively low electrical conductivity
Compression Molded BPP (ICT) 55 wt.% Filler	15,0 – 19,0	0,9 – 2,3	2,0 – 3,0		
Compression Molded BPP (ICT) 68 wt.% Filler		6 - 7	1,2 – 1,8		
Compression Molded BPP (ICT) 77 wt.% Filler		20 - 25	1,2 – 1,8		

For RFB chemical stability has a higher priority than electrical conductivity. As power densities are lower, the ohmic drop at the bipolar plate is mainly governed by contact resistance to the porous electrode.

The same material with higher filling ratios is comparable to commercial PPG86, but with 10% lower carbon fillers

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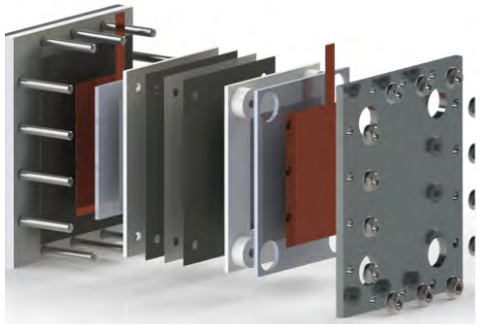
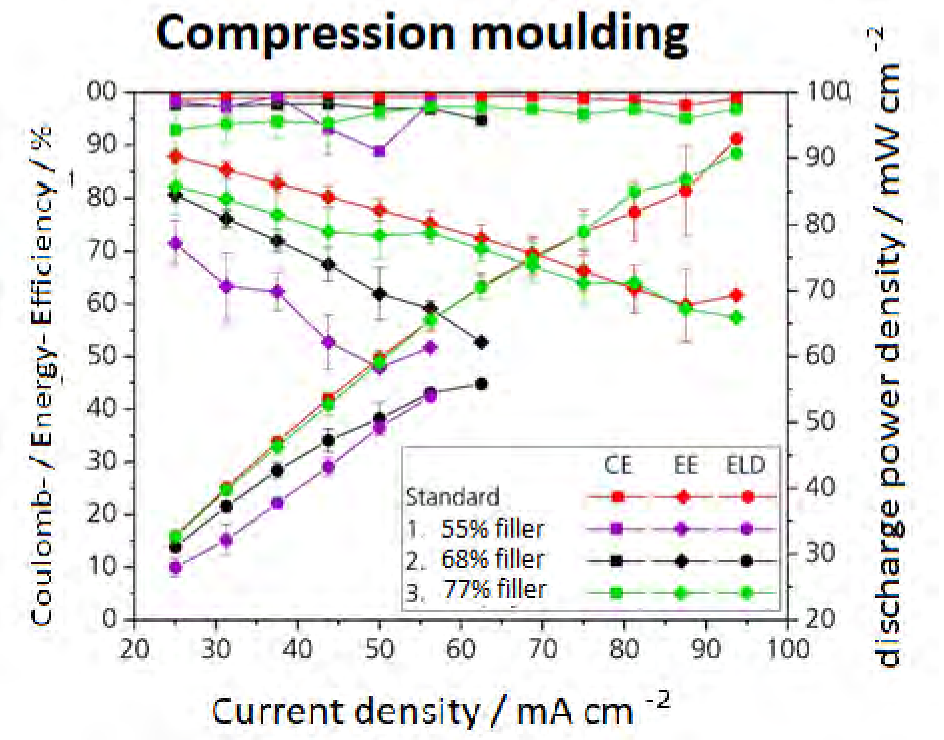
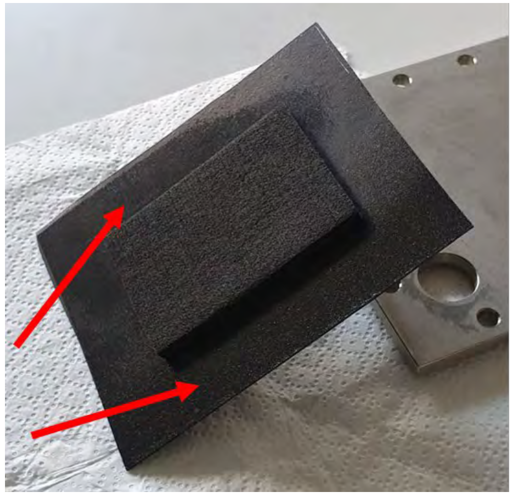
Cell performance and production of laminates

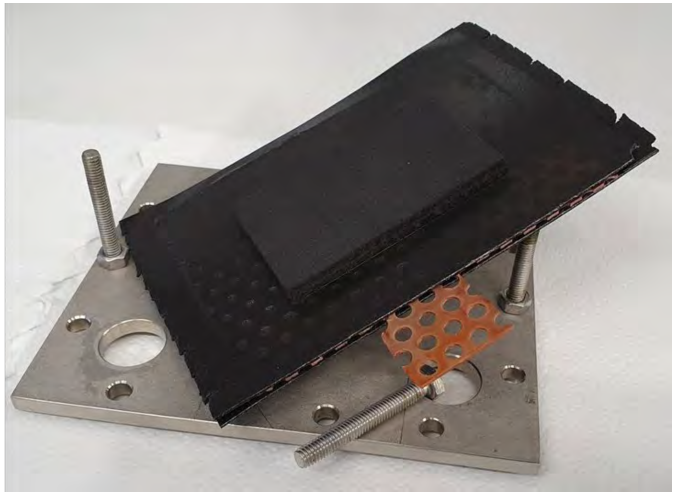


Highest filling grade (77% filler) is comparable to standard material



Reduction of contact resistance by laminates via controlled hoth-pressing





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