



First Project Workshop

In Pilsen and Online

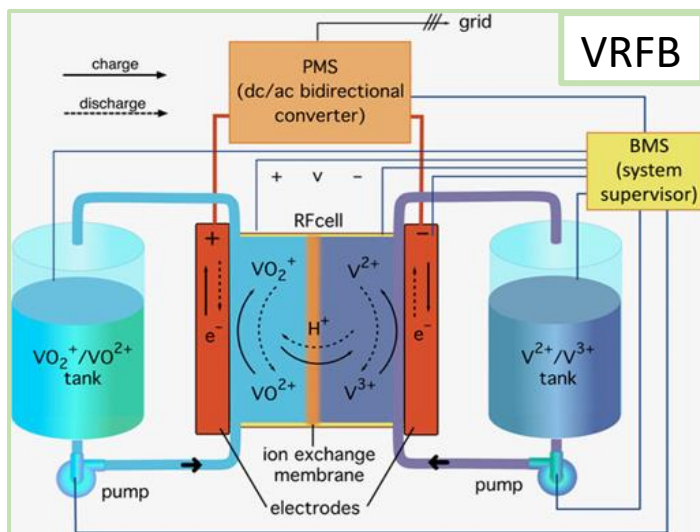
AORFB, from chemistry selection to
electrolyte development

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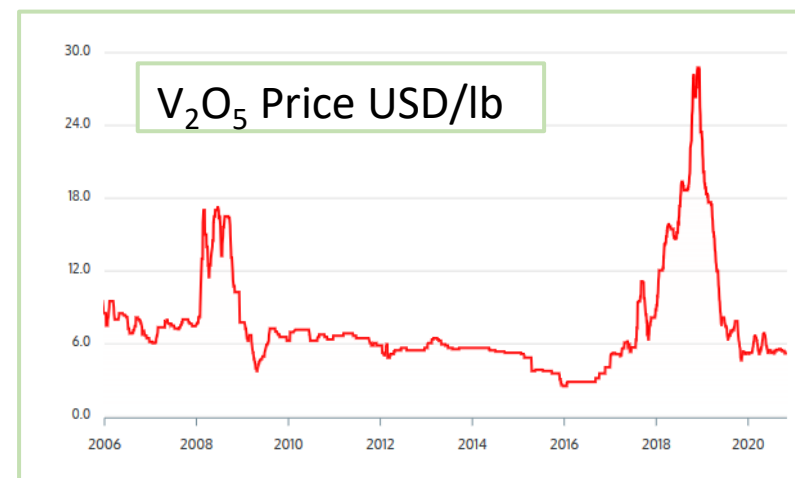


*The research leading to these results has
received funding from the European Union
under Grant Agreement no. 875613*

Why AORFBs?



Strategic material



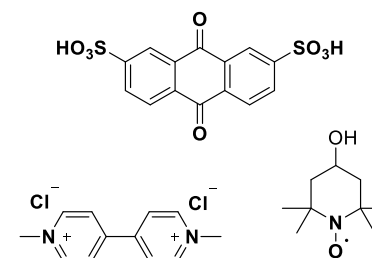
VRFBs	AORFBs
Price/Scarcity	Earth abundant
Limited energy density	Tunable Ered and solubility
Thermal stability	Minimized crossover

ENERGY STORAGE

Redox flow batteries go organic

The use of renewable resources as providers to the electrical grid is hampered by the intermittent and irregular nature in which they generate energy. Electrical energy storage technology could provide a solution and now, by using an iterative design process, a promising anolyte for use in redox flow batteries has been developed.

Wei Wang and Vince Sprenkle



Ideal electrolyte for AORFB – HIGREEW targets

Active materials

- Cost of active material (1-5 €/kg)
- Water solubility (2 eq./L)
- Chemical & thermal stability (T range)
- Redox kinetics ($> 10^{-3}$ cm/s)
- Cell voltage ($> 1V$)

SET plan targets

- LCOS (0,05€/kWh/cycle at 10.000 cycles)
- Scalability/safety/environmental impact

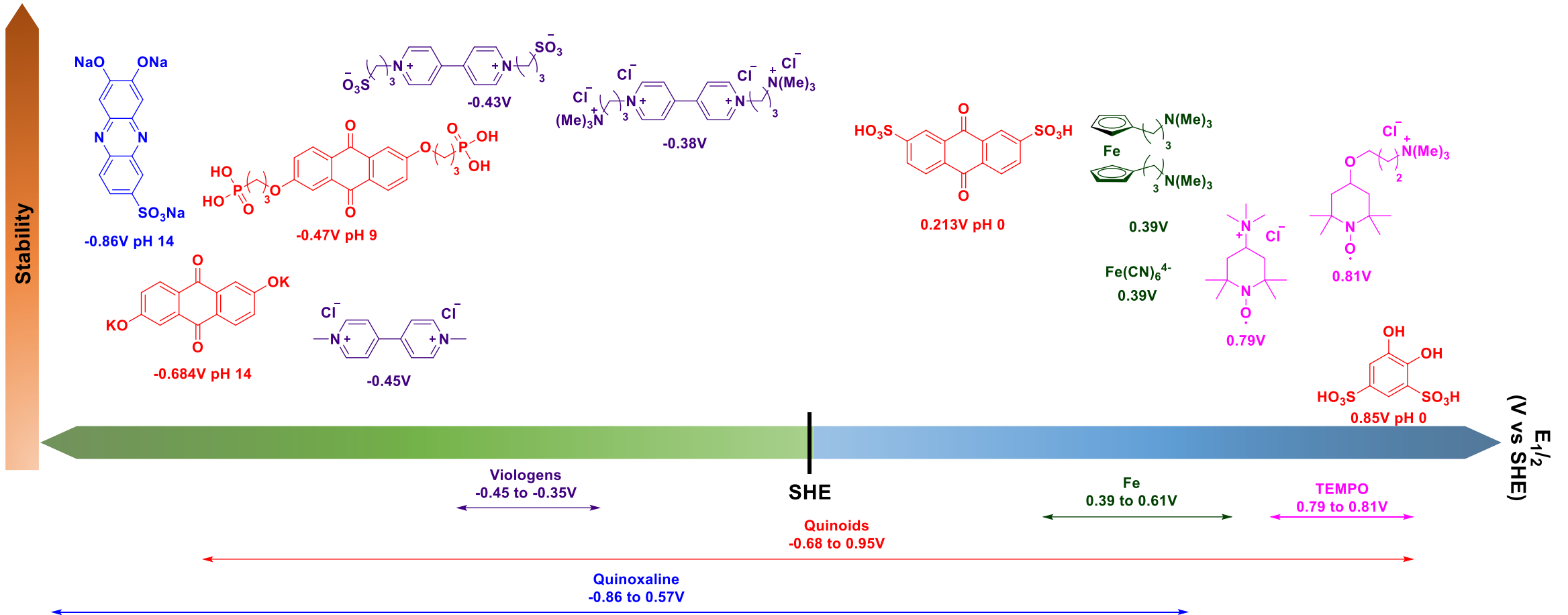
Electrolyte – battery

- Energy cost (< 50 €/kWh)
- Energy density (> 30 Wh/L)
- Capacity retention (8.000 cycles)
- Efficiency
 - Conductivity $> 0,1$ S/cm
 - Viscosity: < 10 cP
 - pH: neutral pH

Planning

1. Design & synthesis of active materials
2. Electrochemical characterization
3. Scale-up process & electrolyte development

Design & synthesis of active materials

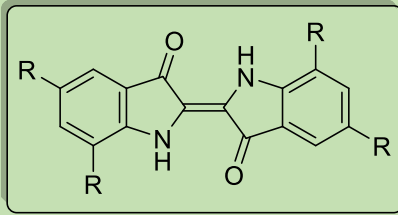


Viologens as anolyte & TEMPO and Fe-based catholytes

Screening of active materials

24 compounds synthesized

A) INDIGO

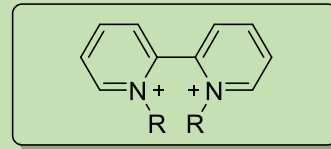
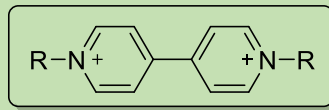


6 compounds



- Ring substitution (SO_3R)
- Counterion effect on solubility ($^+\text{NR}_4$ cations)

B) VIOLOGEN

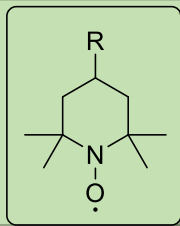


11 compounds



- DFT / substituent effect
- N position / N substitution ($^+\text{NR}_4$, SO_3^-)
- Ring substitution (Ph, Me, OMe, COOH)

C1) TEMPO

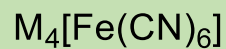


3 compounds

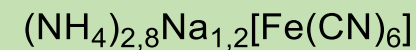


- Ring substitution pattern – position 3 vs 4
- Substituents ether, amine and alkyl linkers

C3) FeCN



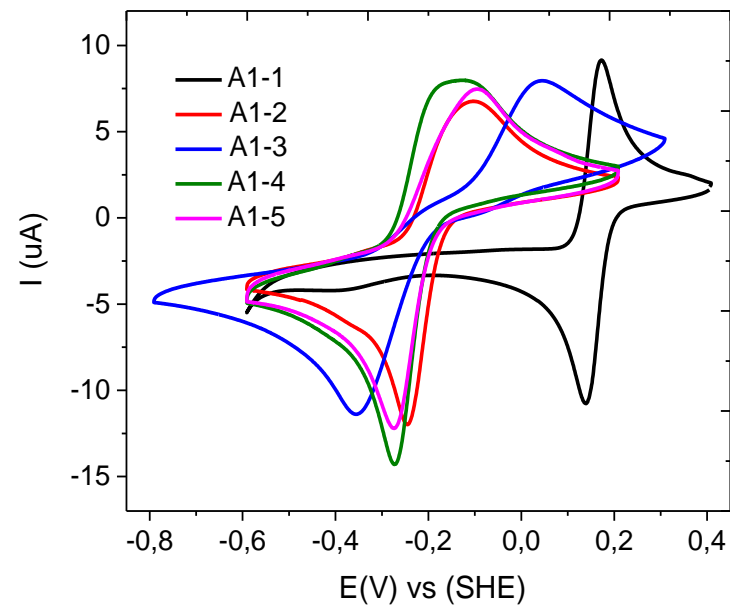
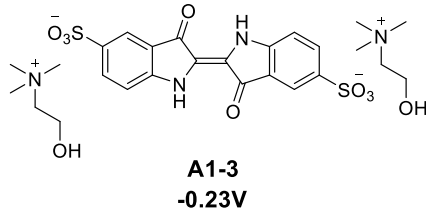
4 compounds



- Cation exchange process
- Multiple cation salts

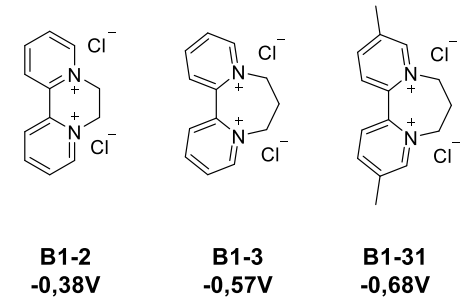
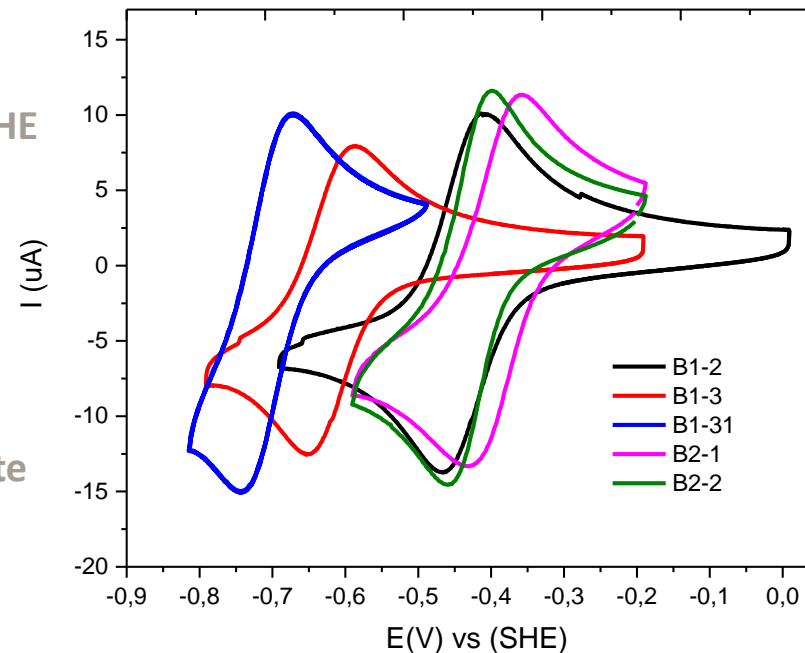
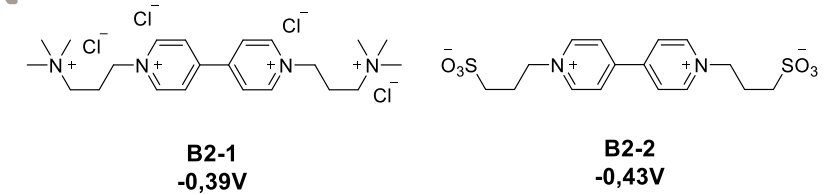
Indigo derivatives: electrochemical characterization

INDIGO



- Stable cycling at pH 7
- $E_{red} = -0,23$ to 0 V vs SHE
- Fast reaction kinetics
 $k = 10^{-3}$ cm/s
- Diffusion coefficients
 $D = 10^{-6}$ cm²/s
- Non-reversible catholyte

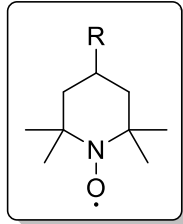
VIOLOGEN



- Stable cycling at pH 7
- $E_{red} = -0,7$ to $-0,4$ V vs SHE
- Fast reaction kinetics
 $k = 10^{-2}$ cm/s
- Diffusion coefficients
 $D = 10^{-6}$ cm²/s

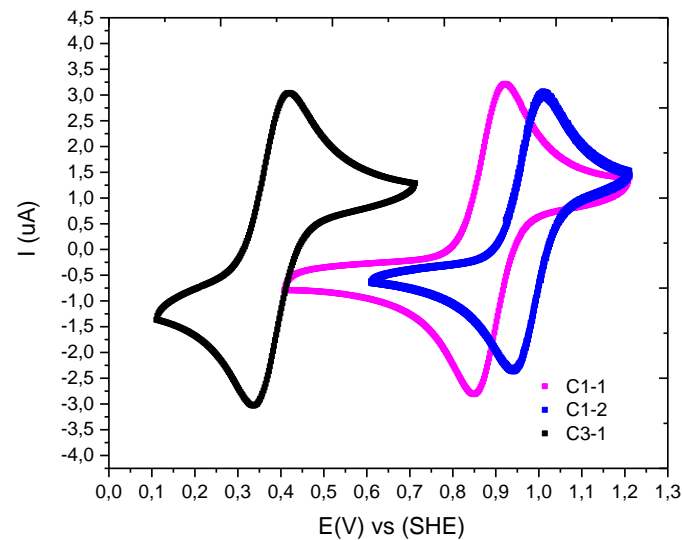
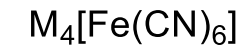
Catholytes: electrochemical characterization

TEMPO



- Not all materials showed stable cycling
- C1-2 unstable: MsO^- anion /short linker
- $E_{\text{red}} = 0,8 \text{ to } 0,98 \text{ V vs SHE}$
- Fast reaction kinetics $k = 10^{-2} \text{ cm/s}$
- Diffusion coefficients $D = 10^{-6} \text{ cm}^2/\text{s}$

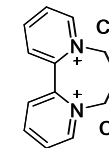
FeCN



- Not all materials showed stable cycling
- No effect of cations on E_{red}
- $E_{\text{red}} = 0,39 \text{ V vs SHE}$
- Fast reaction kinetics $k = 10^{-3} \text{ cm/s}$
- Diffusion coefficients $D = 10^{-6} \text{ cm}^2/\text{s}$

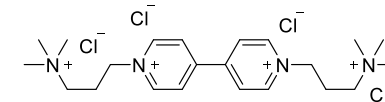
Cell testing: viologen-TEMPO system

- CV studies: Viologen B1-3 and TEMPO based C1-1 redox pair - Cell voltage 1,46 V
- Single cell testing: B1-3 unstable – promotes fast capacity decay
- Single cell testing: B2-1 and C1-1 lead to stable cycling (<0,01%/cycle for 1,28 V cell voltage)

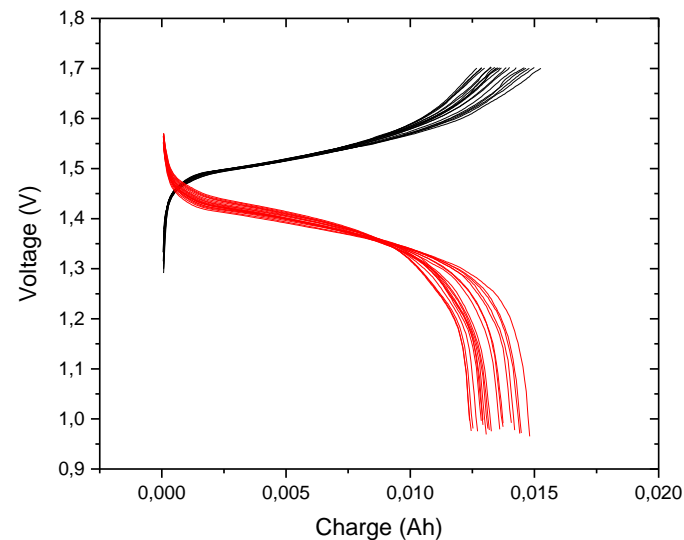
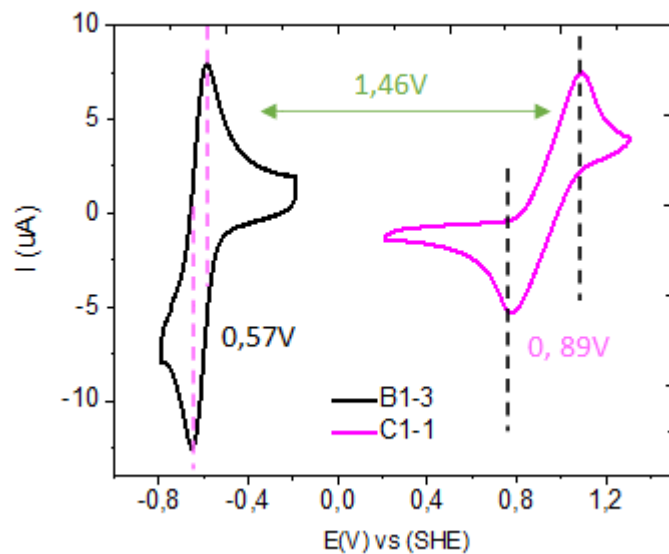


B1-3
-0,57V

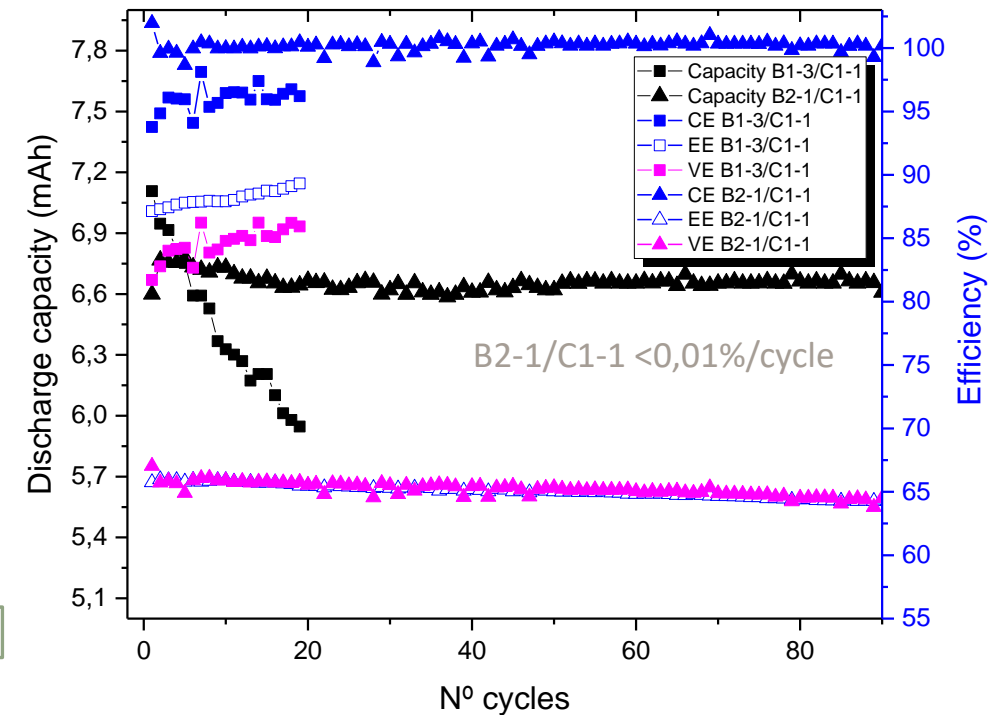
VS



B2-1
-0,39V

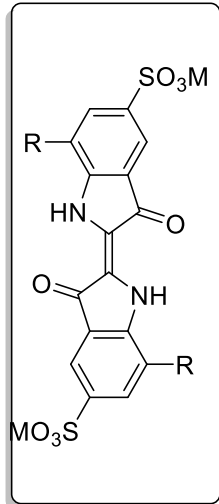


25 mM B1-3 in 0,5M NaCl; 25 mM C1-1 in 0,5M NaCl (40 mA/cm²)



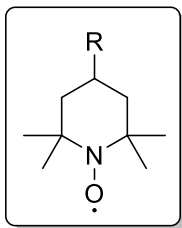
Characterization summary

A: Indigo-based

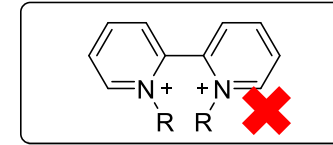
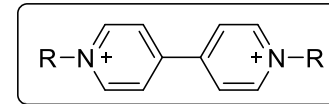


- Kinetics (10^{-3} cm/s) ●
- Solubility (1 mol e-/L) ●
- Redox potential (-0,2 V) ✗
- Viscosity (1 P) ✗
- Bifunctional ✗
- Straightforward synthesis ●

C1: TEMPO-based



- Kinetics (10^{-2} cm/s) ●
- Solubility (2-3 mol e-/L) ●
- Redox potential (0,8 to 0,94 V) ●
- Viscosity (1-10 cP) ●
- Straightforward synthesis ✗
- Stability ●



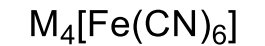
B: Viologen-based



- Kinetics (10^{-2} cm/s) ●
- Solubility (2-2,6 mol e-/L) ●
- Redox potential (-0,4 to -0,7 V) ●
- Viscosity (1-10 cP) ●
- Straightforward synthesis ●
- Stability (4,4'-bipyridinium salts) ●

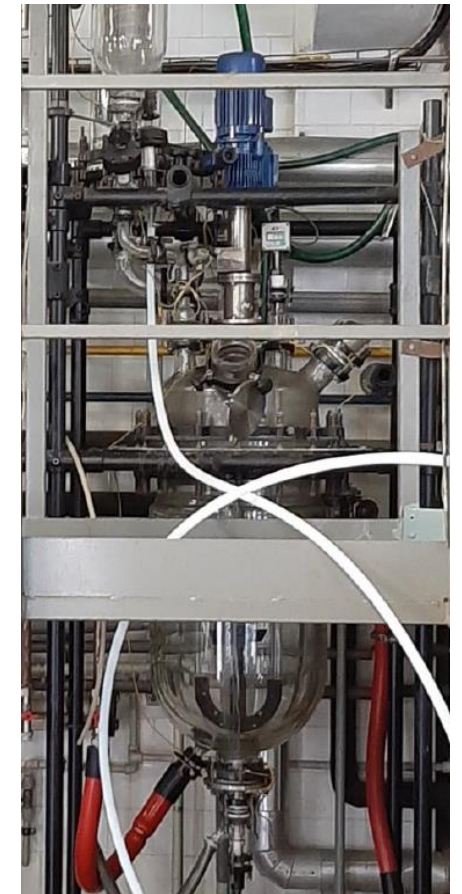
- Kinetics (10^{-3} cm/s) ●
- Solubility (1,2 mol e-/L) ●
- Redox potential (0,4 V) ●
- Viscosity (1-2 cP) ●
- Straightforward synthesis ●
- Stability ●

C3: Ferrocyanide based

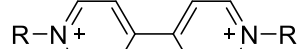
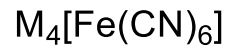
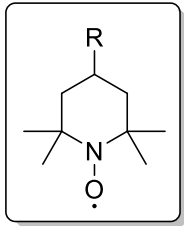


Scale-up process: Transfer from lab to pilot

- **Chemicals (toxic, volatile, explosive, carcinogenic, etc.)**
 - Reagents feasible at lab scale, may pose problems at bigger scale
 - Solvents have to be redefined: a) safety/legal regulations; b) operation purposes; c) recovery; d) cost
- **Synthetic routes**
 - Minimum number of steps and high yields
 - Atom economy
 - Convergent synthesis
- **Operation conditions**
 - Temperature
 - Purification techniques
 - Engineering aspects
 - Anion/cation exchange columns

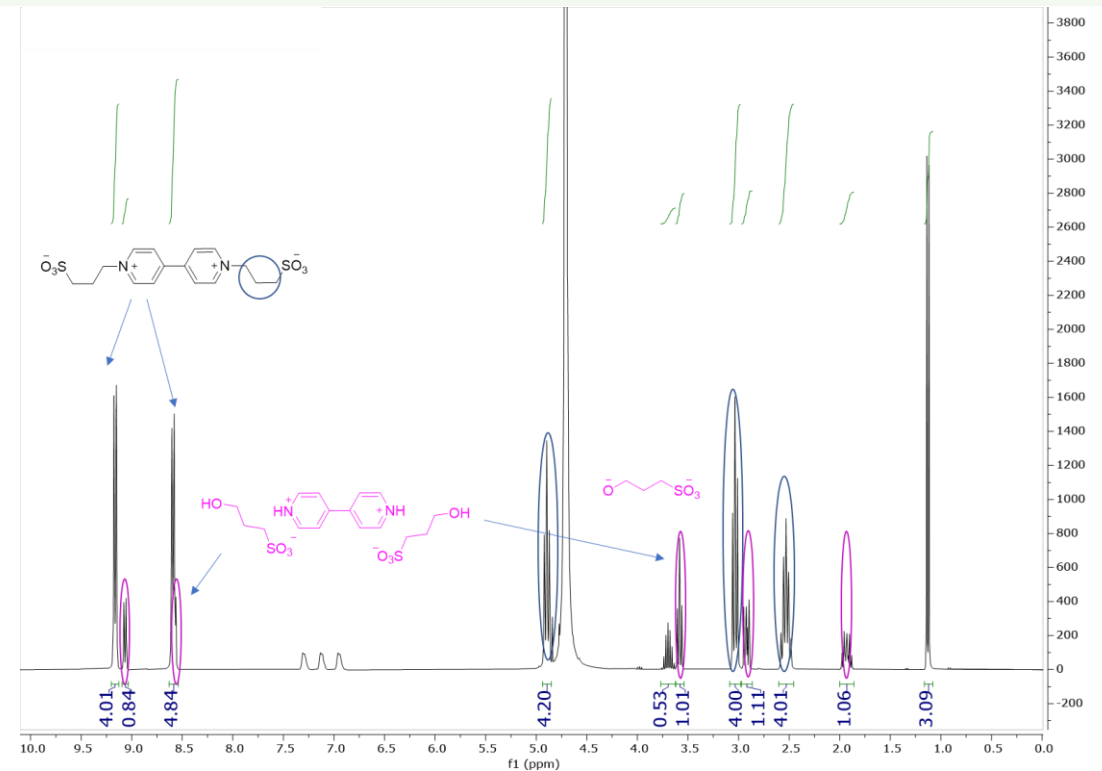
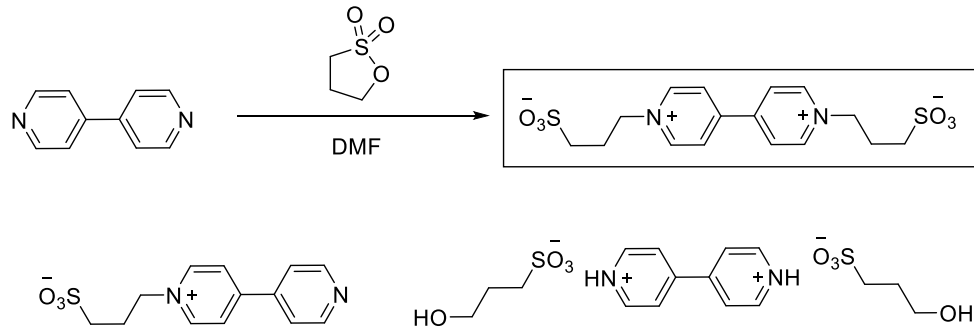


Scale-up process: Transfer from lab to pilot

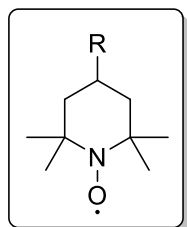


• Viologen compounds ●

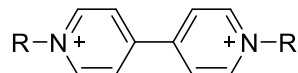
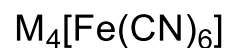
- Straightforward synthesis from bipyridine – product isolated as solid
- DMF was replaced by alternative high boiling point, non-toxic solvents (ROH, Aromatics)
- Efficiency of the reaction – critical in the purity of final product (> 95%)



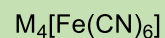
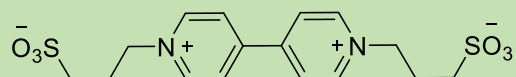
	EIS - ohmic resistance (Ohm.cm2)		
SOC	0.1	0.5	0.9
CIC	1.34	1.24	1.12
COC1	2.92	2.12	1.36
COC2	1.56	1.3	1.16



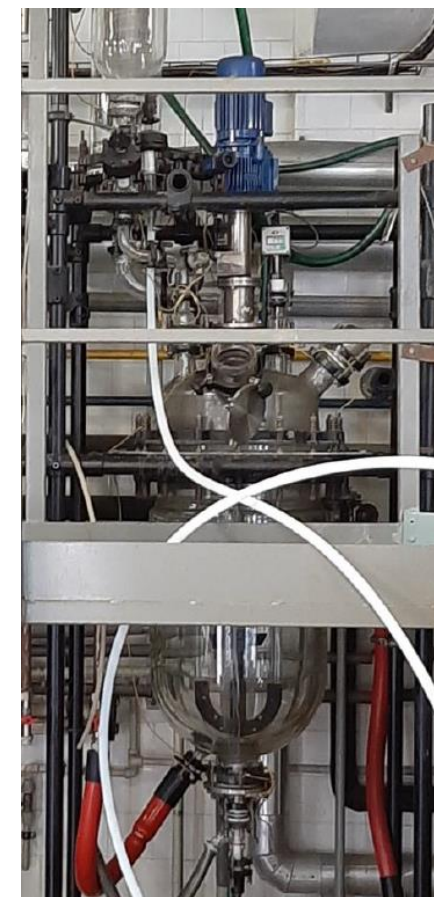
Scale-up process: Transfer from lab to pilot



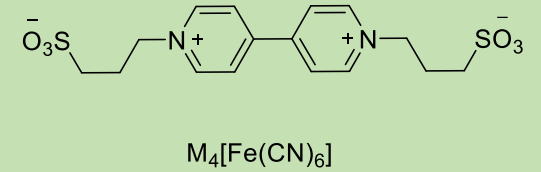
- High redox potential TEMPO derivatives ❌
 - High performance compounds required 4-6 reaction steps
 - Complex purification techniques (chromatography)
- Ferrocyanide based compounds ●
 - Already existing industry for ferrocyanide production
 - Straightforward synthesis
 - Water evaporation – undesired / tedious process



25 €/kWh



Electrolyte formulation – Starting point



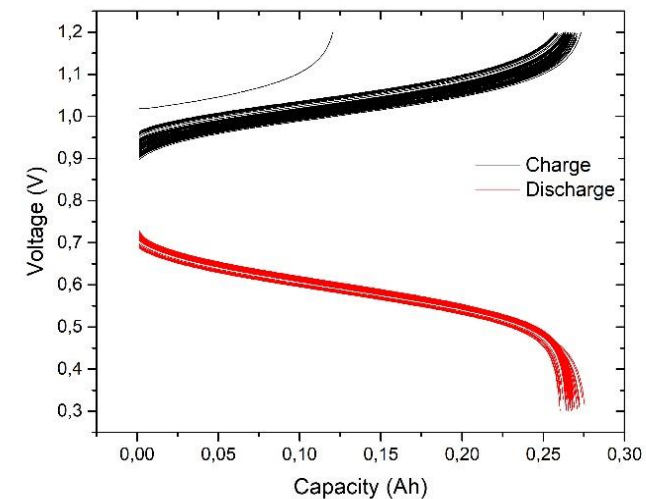
- Active materials are main but not only component of electrolytes

- pH, supporting electrolyte salts, charge carriers
- Temperature, SoC & operating conditions

- Screening

- Concentration/solubility f(T): fixed as 0,9M B2-2 and 0,9M C3-1
- Supporting electrolyte: defined as pH 7 and NH_4Cl as carrier salt
- Concentration of carrier salt (0-3 M NH_4Cl) – ionic strength
- Impact of composition on:
 - Thermal stability: NH_4Cl and $(\text{NH}_4)_x\text{M}_{4-x}[\text{Fe}(\text{CN})_6]$ 0-45°C
 - Conductivity and efficiency
 - Crossover: water transport depends on SoC/Ionic strength/T

Active Material (M)	Supp. Electrolyte (M)	σ (mS cm ⁻¹) (25°C)	η (cP) (25°C)
B2-2 (0.9M)	NH_4Cl (1.0M)	51	3.2
B2-2 red (0.9M)	NH_4Cl (1.0M)	78	4.5
B2-2 (0.9M)	NH_4Cl (1.5M)	62	3.2
B2-2 (0.9M)	NH_4Cl (2.0M)	79	3.2
B2-2 (0.9M)	NH_4Cl (3.0M)	110	3.5
C3-1 (0.9M)	NH_4Cl (1.0M)	324	1.4



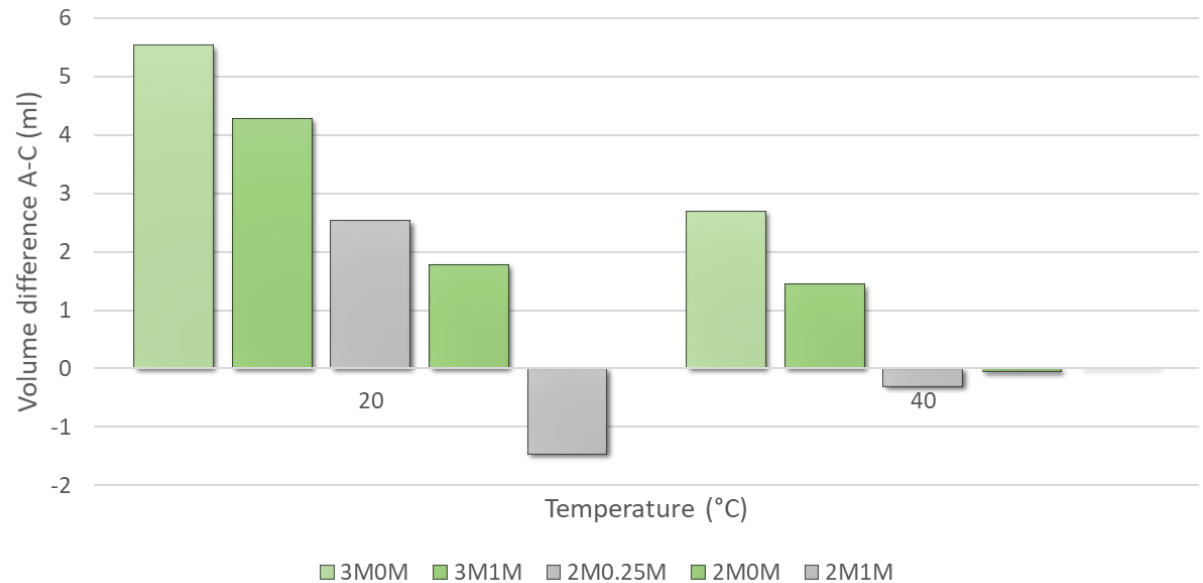
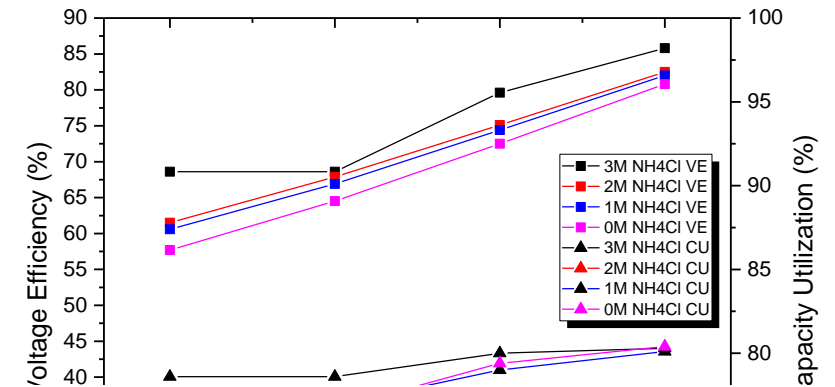
Electrolyte formulation – Start point – Beyond AM

- Active materials are main but not only component of electrolytes

- pH, supporting electrolyte salts, charge carriers
- Temperature, SoC & operating conditions

- Screening

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Conclusions

- Development of electrolytes is a long way from chemistry selection and should be adapted throughout different stages
- Active material defines electrochemistry – but there is much behind
- Scale-up process is a critical role in the irruption of new chemistries
- Variety of active materials (>20) & two electrolyte solutions developed
 - High performance electrolyte (1.3 V; < 0,01%/cycle) based on highly soluble active materials
 - Cost competitive (25 €/kWh) electrolyte (0,8 V; < 0,01%/cycle, up to 77% EE)

STILL TO COME

- Successfully integrate electrolytes in HIGREEW stacks

Thank you!



*The research leading to these results has
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