Second Project Workshop

Vitoria-Gasteiz

HIGREEW Project a journey through new generation AORFB

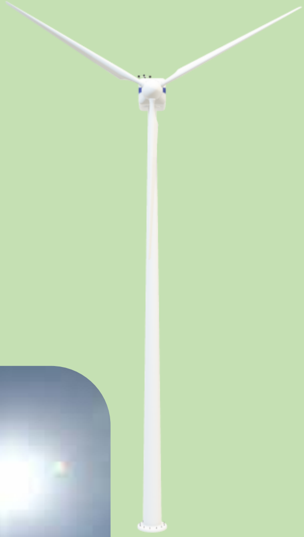
Eduardo Sánchez Díez (CICe)

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

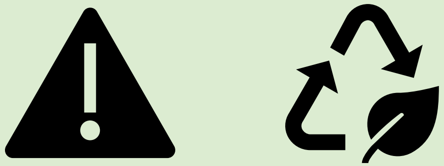
Next generation RFB

Levelized cost of storage

- Materials cost
- Production cost
- Performance
- Maintenance cost
- End of life management cost



Environmental impact & Safety



- Raw materials production/extraction
- Battery components production
- Battery construction – operation and end of life management
- Battery efficiency
- Toxicity of components
- Operation risks

Availability of materials & Mass production

- Scalability of production processes
- Geopolitics
- Global distribution of resources
- Recyclability
- Finite resources

Stepwise process – chemistry centered development

- **Chemistry and electrolyte selection**
- Cell and cell components definition
- Stack design and construction
- BoP and system design

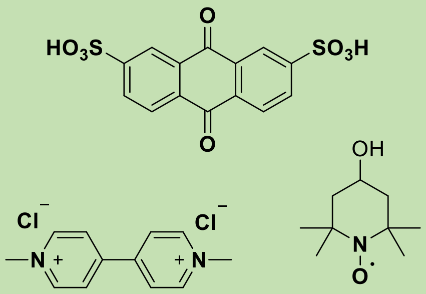
ENERGY STORAGE

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

- Voltage
- Energy density
- Stability
- Performance
- Cost
- Environmental impact
- …

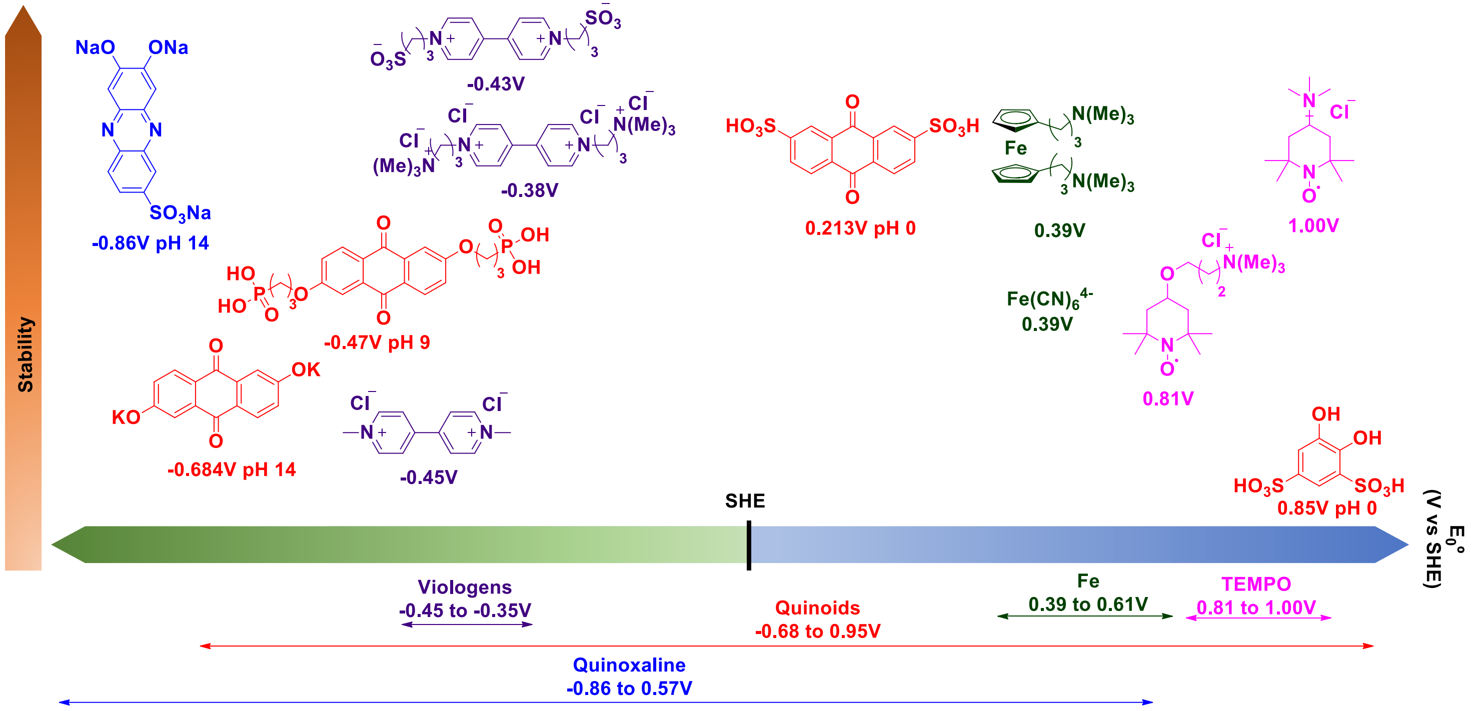


HIGREEW approach

HIGREEW

Targets

- Neutral pH electrolyte
- Broaden cell voltage (> 1V)
- High water solubility (2 eq/L)
- New materials
- High stability
- Low cost of active material (1-5 €/kg)

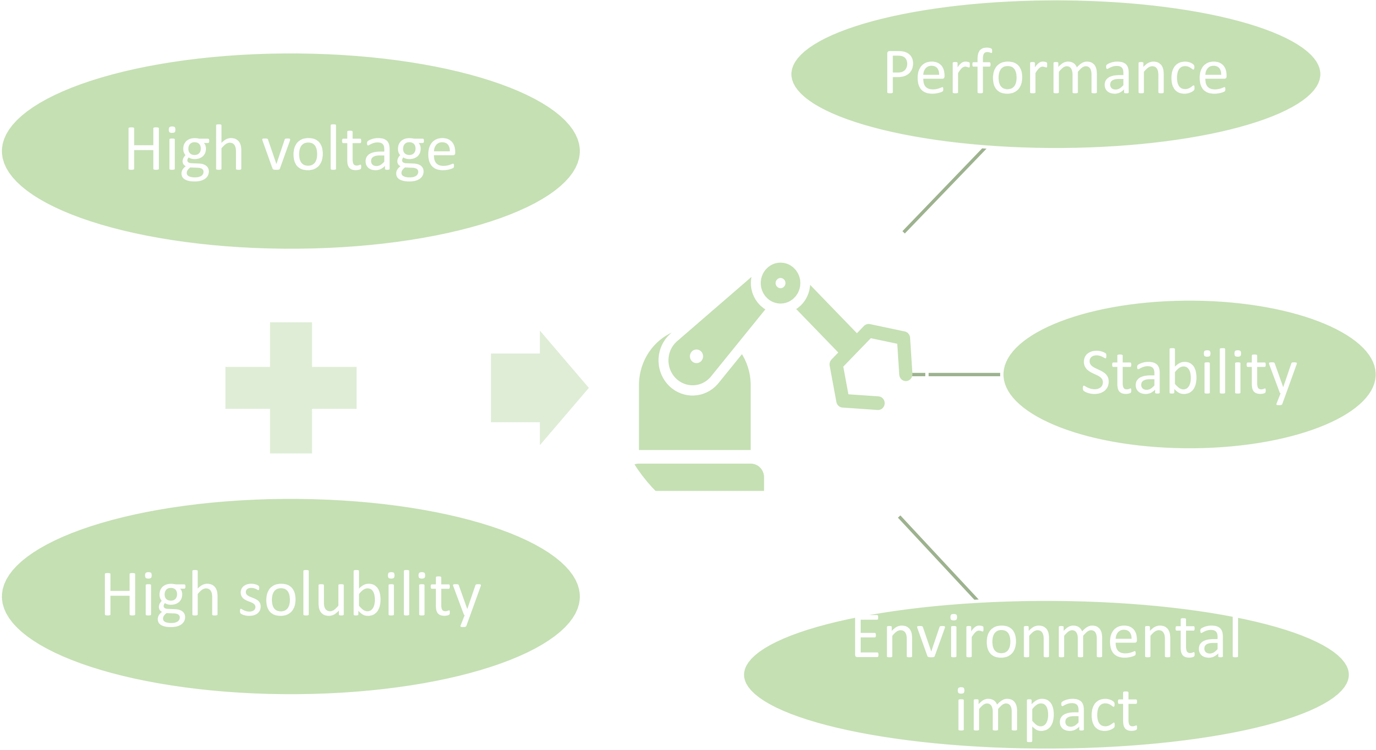


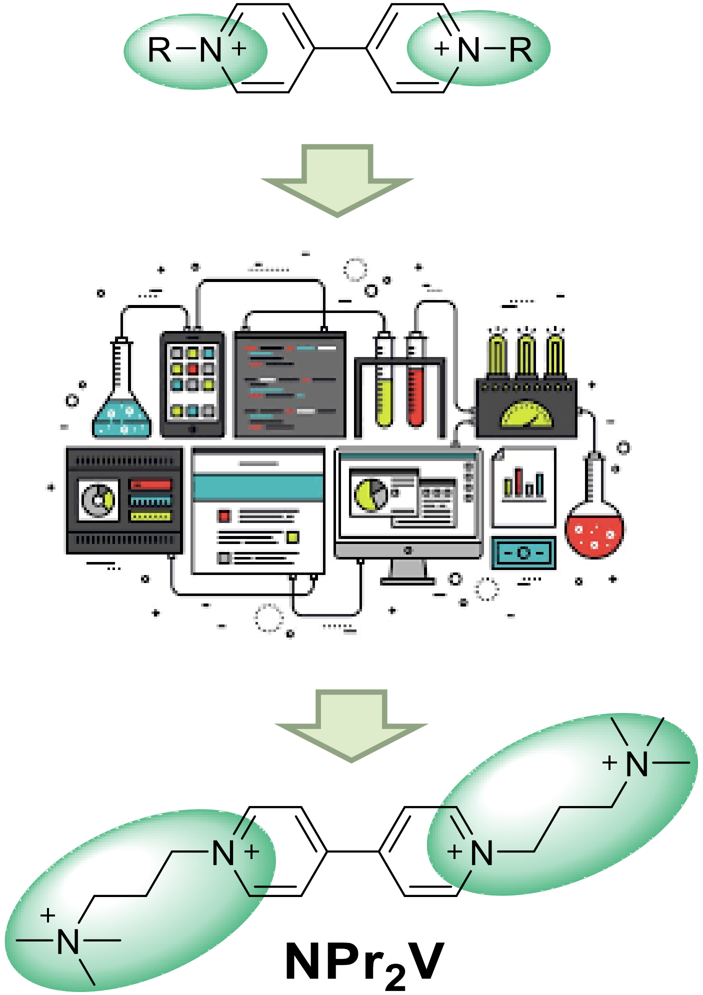
Viologen-TEMPO

Viologen-ferrocyanide

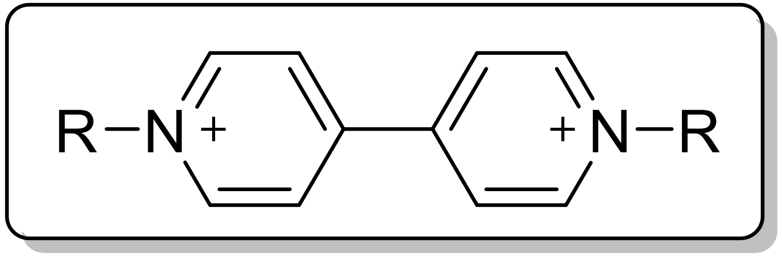
New design

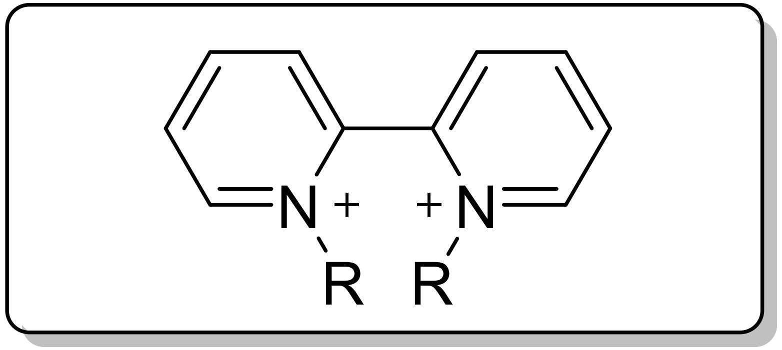
HIGREEW

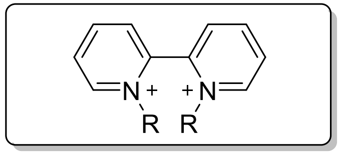




New viologen type materials



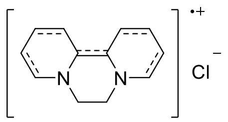


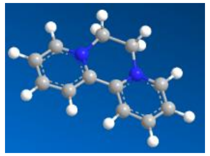


Design & synthesis

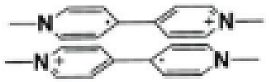
- Planar flexible structure

PROS
Inter-ring delocalization



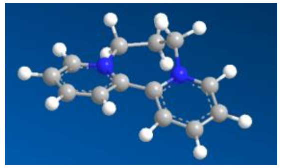


CONS
Stacking & dimerization

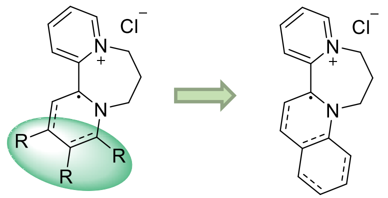


- Non-planar flexible structure

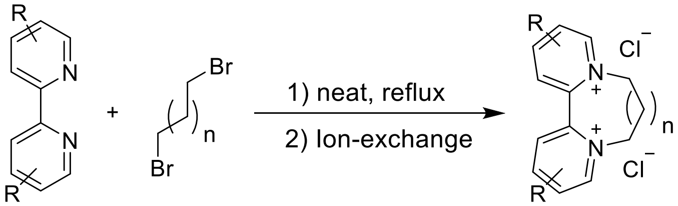
PROS
Increased solubility
Avoid dimerization



Extended intra-ring delocalization

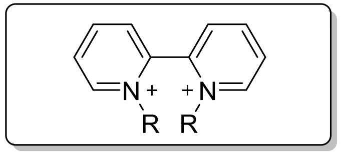


- Straightforward synthesis

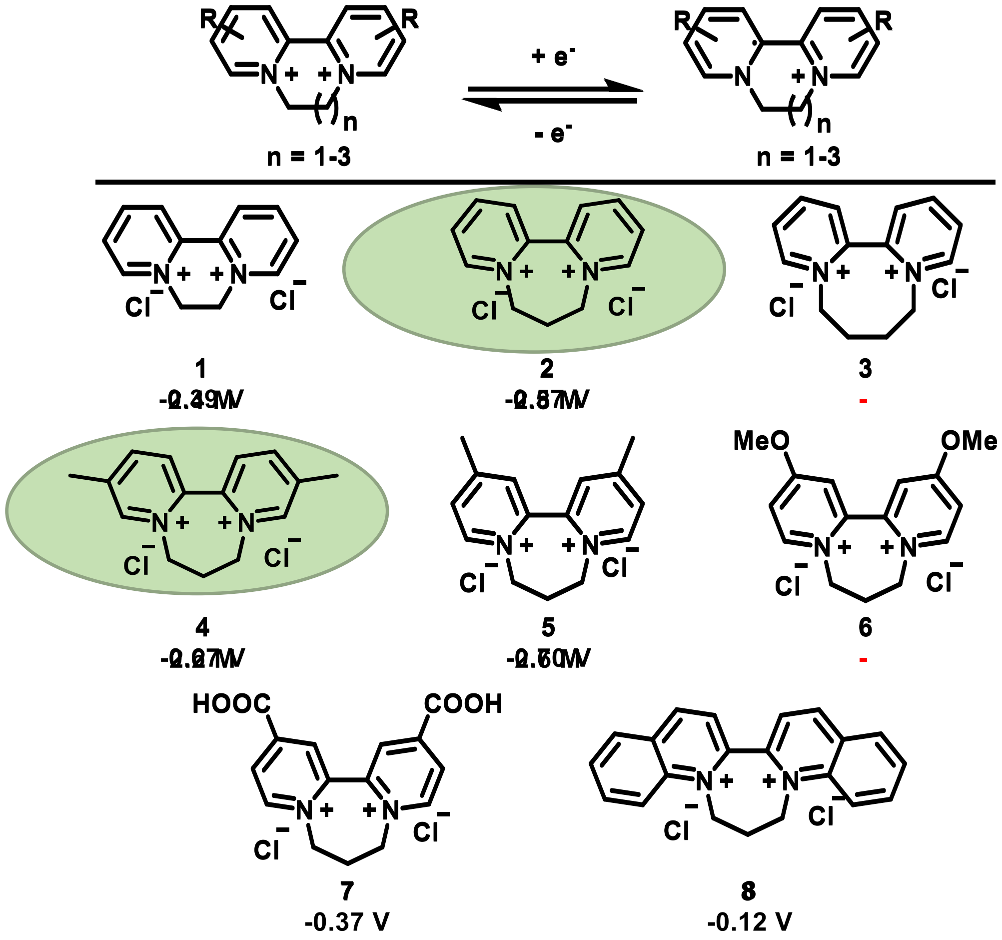


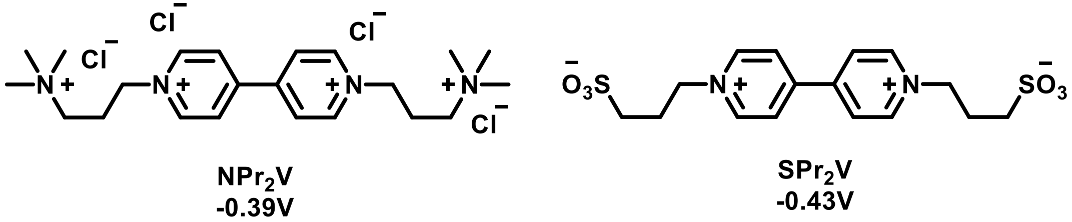
8 compounds

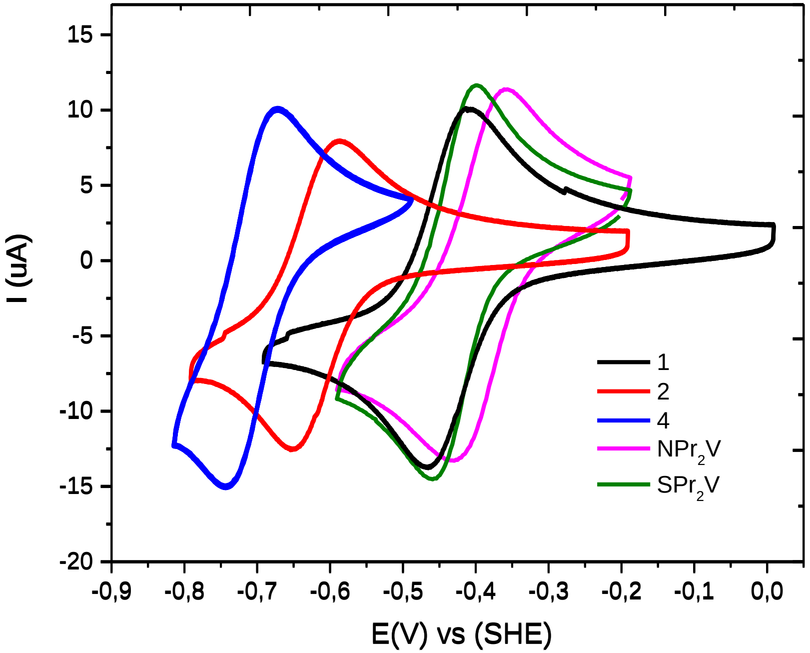
2,2'-bipyridinium salts



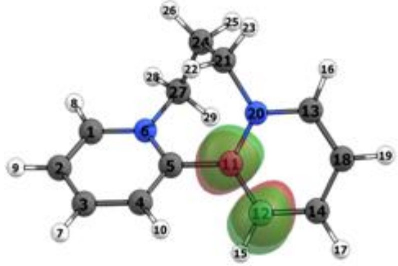
Performance characterization







- Fast reaction kinetics $k = 10^{-2}$ cm/s
- Diffusion coefficients $D = 10^{-6}$ cm²/s
- Ered = -0.7 to -0.4 V vs SHE



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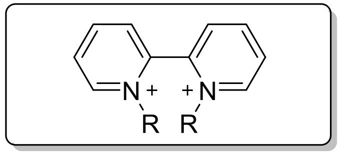
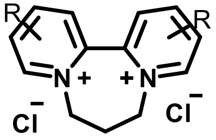
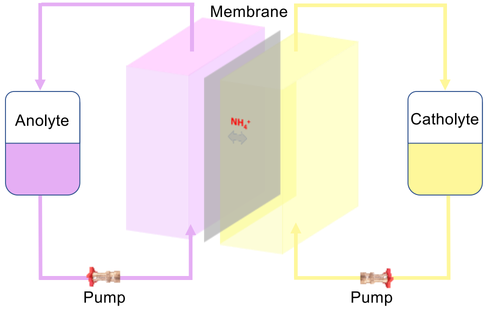
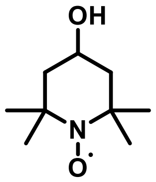
2,2’-bipyridinium salts

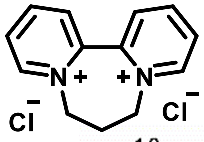


Performance characterization

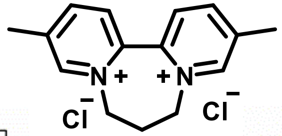






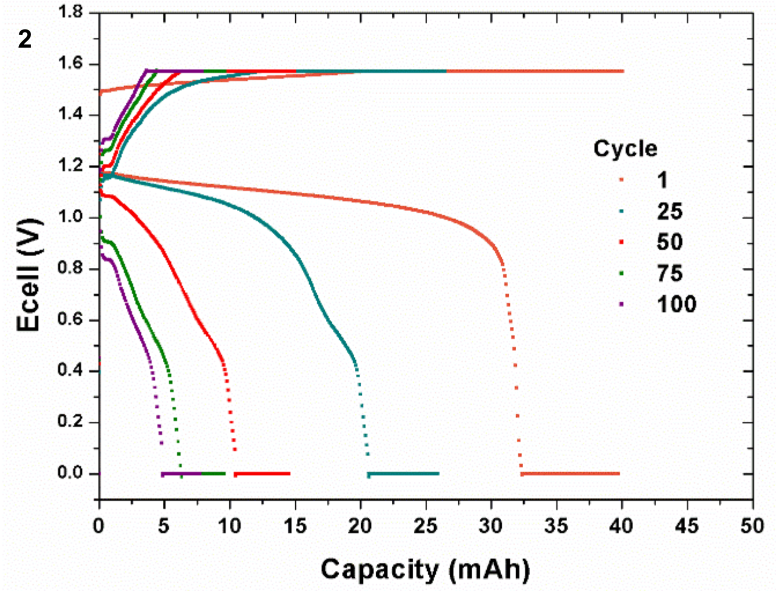


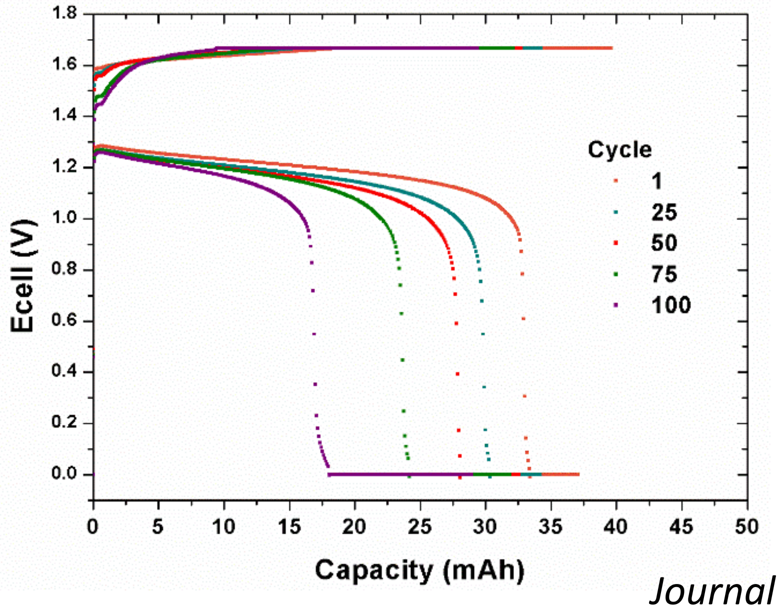
2



4

100 cycles
0.1 M anolyte / 0.15 M TEMPOL
100 mA/cm^2 - CCCV
FAA-3-50 / GFD 4.6EA





- Fast capacity decay
- Higher stability of methyl substituted compound 4 (0.16%/cycle) vs compound 2 (0.75%/cycle)
- Good agreement of computational and experimental results.
- Structure and performance relation identified
- Chemical degradation identified, main subproduct protonated reduced viologen

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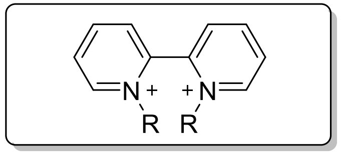
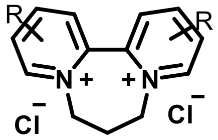
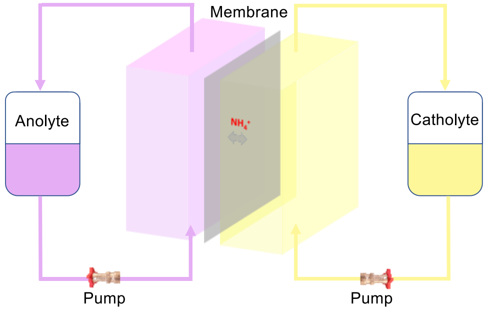
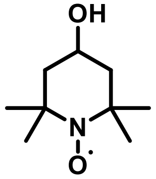
2,2’-bipyridinium salts

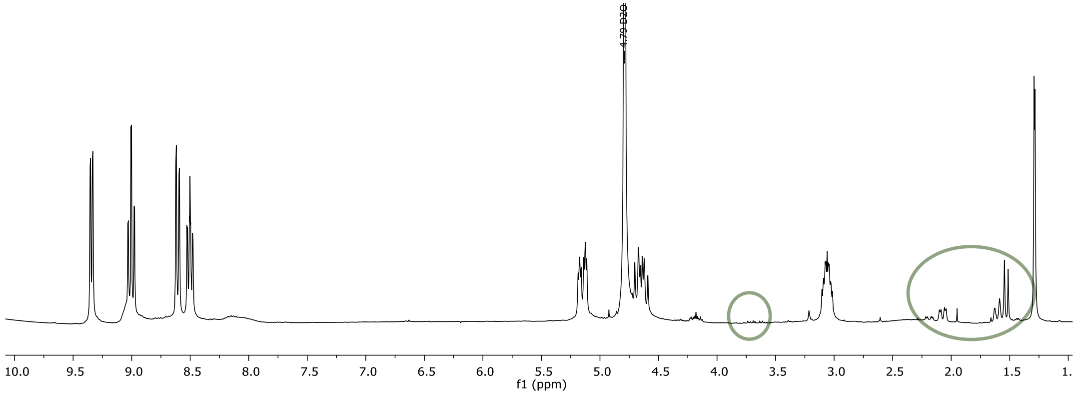


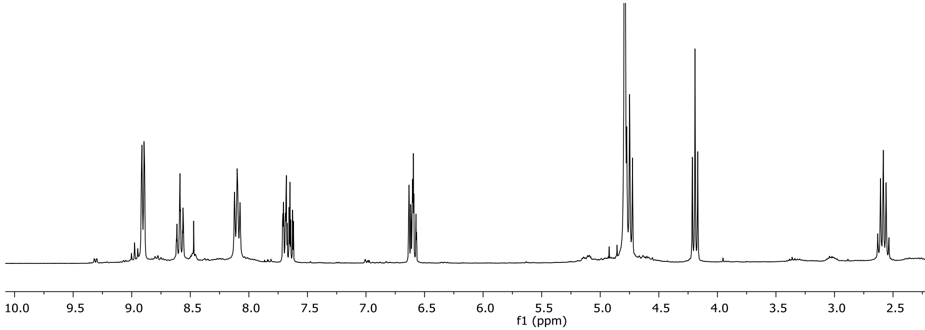
Performance characterization

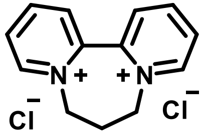












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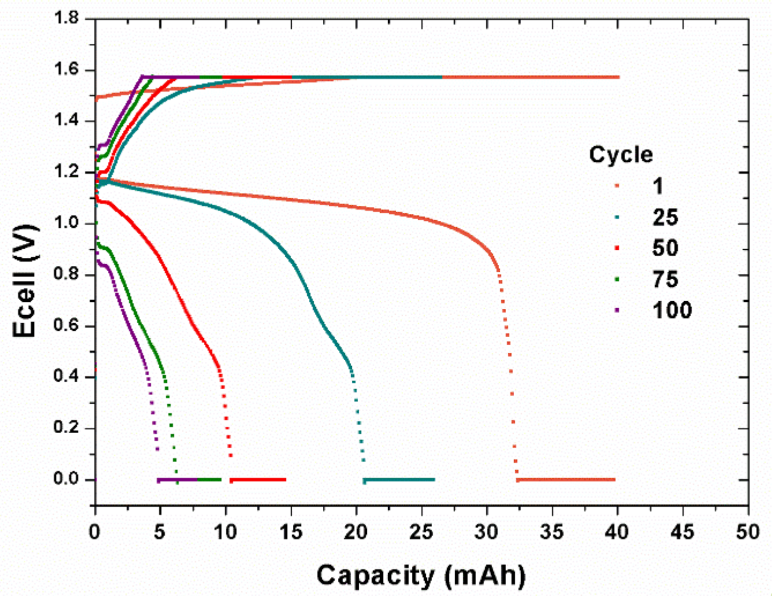

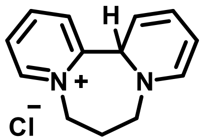

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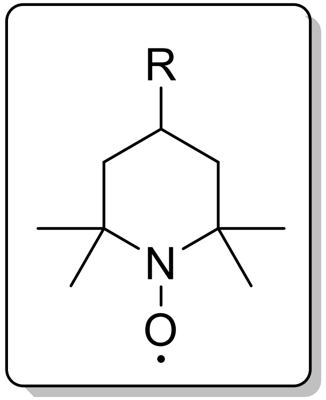
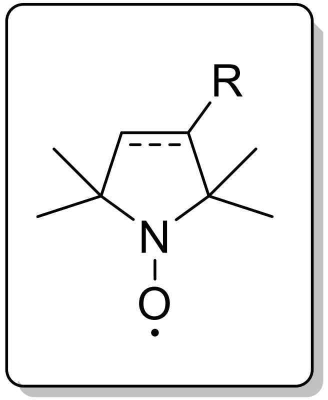
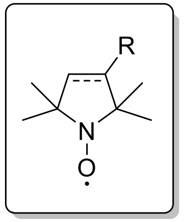
New TEMPO type materials

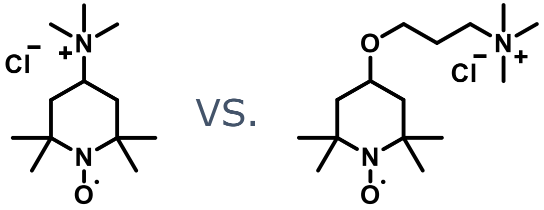




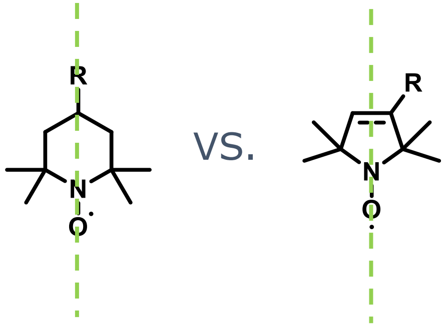


Design & synthesis

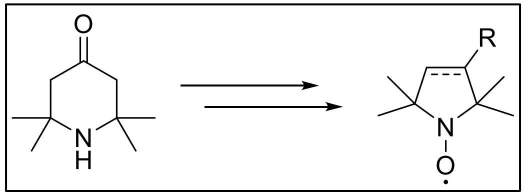
- Influence of the EWG – hydrophilic group and spacer



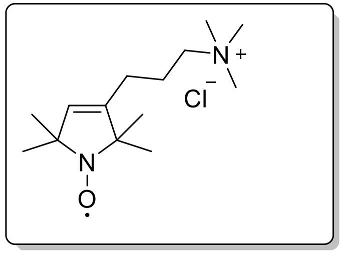
- Non-symmetric structure: increased solubility



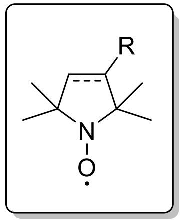
- New synthetic route – new family of catholyte active materials



4 compounds

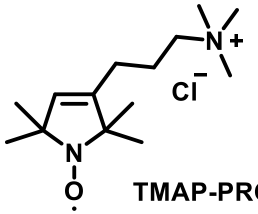


Manuscript in preparation

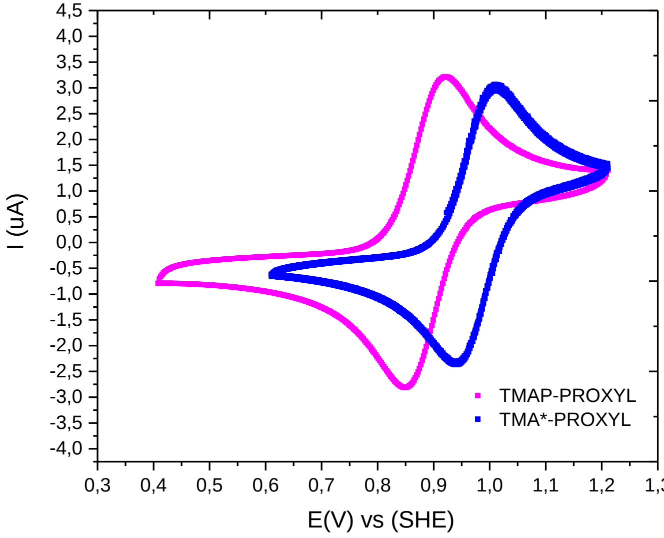


Proxyl derivatives

Performance characterization



TMAP-PROXYL



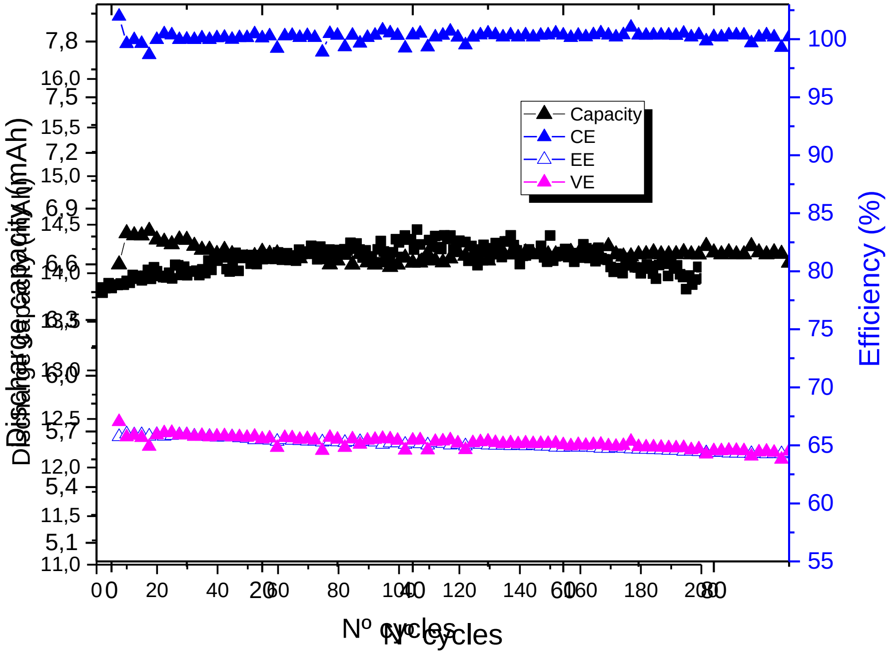
Synthetic Nitroxyl

200 cycles

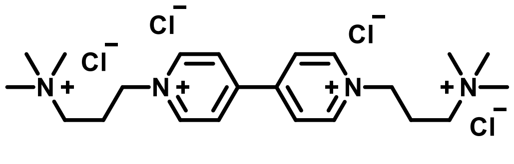
0.5 M / 25 mM

40 mA/cm²

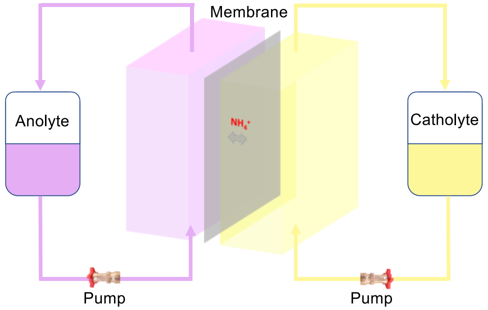
FAA-3-50 / GFD 4.6EA

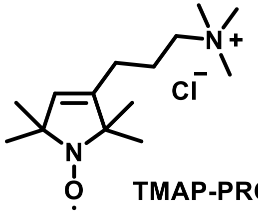


- Fast reaction kinetics k = 10^{-2} cm/s
- Diffusion coefficients D = 10^{-6} cm^2/s
- Ered = 0.9 to 1.0 V vs SHE



NPr_2V
-0.39V





TMAP-PROXYL

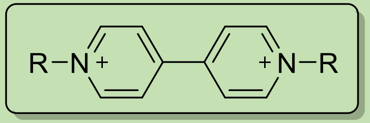
- High cycling stability. Negligible capacity decay in 200 cycles
- High cell voltage when couple with NPr_2V >1.3 V

Manuscript in preparation

Scalability & cost analysis

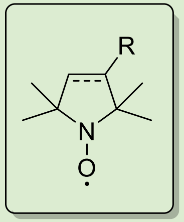
Viologens

- Straightforward synthesis
- 2,2’ bipyridinium salts are not competitive
- Ion exchange resins – complex process
- Available and low cost raw materials
    - Component A (>100 €/kg): Bipyridine (economy scale)
    - Component B (<10 €/kg): Propanesultone, halopropyl trimethylammonium halide (paper industry)
- Cost projections (< 1€/kg)



Nitroxyl radicals

- Synthesis route should be adapted
- High potential electrolyte
    - Voltage 1.3 V
    - Solubility > 2 M (25-35 Wh/L)
    - Stability (< 0.01%/cycle)
- Fully organic catholyte solution
- Cost projections (<5€/kg raw materials)

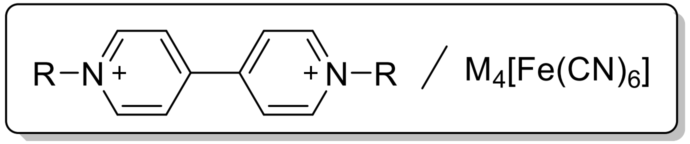


Ferrocyanide

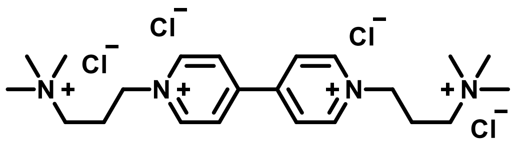
- Mass production ongoing
- Low cost raw materials (1-3 €/kg)
- Highly stable material
- Lower cell voltage < 1V

$M_4[Fe(CN)_6]$

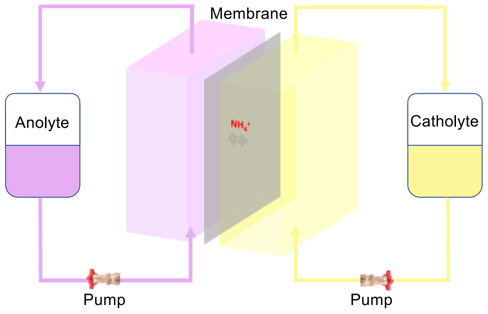
Viologen-ferrocyanide



Final solution for Integration



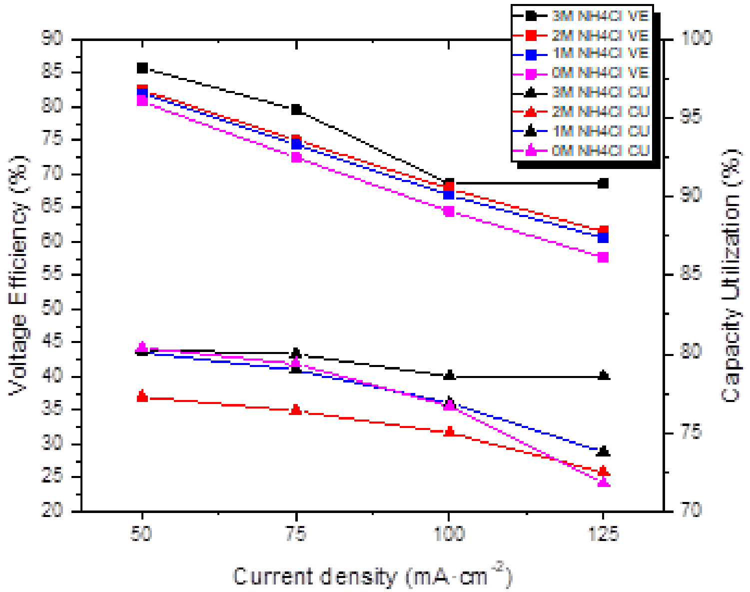
NPr_2V
-0.39V

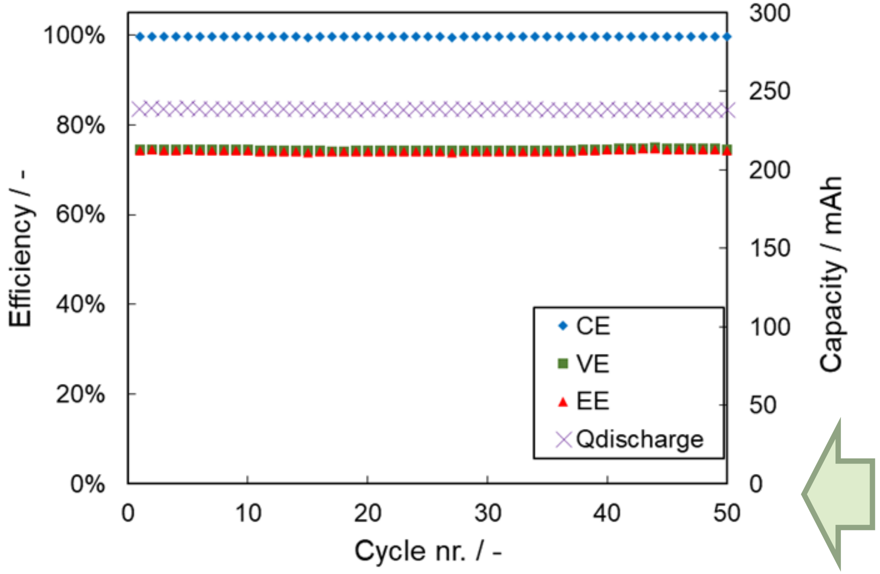


$M_4[Fe(CN)_6]$

- AM & Supp Electr concentration
- Nature of ions (NH_4, K)
- Non-symmetric composition-behaviour

- Energy density
- Ionic strength
- Conductivity
- Thermal stability
- Viscosity
- Cycling stability
- Membrane selection
- Cell design
- System design (BoP)





50 cycles

0.65 M 100 mA/cm²

FS730 / GFD 4.6EA

Conclusions

- Variety of active materials have been developed and integrated as electrolytes
  - High performance electrolyte (1.3 V; < 0,01%/cycle) based on highly soluble active materials
  - Robust and scalable electrolyte (0.8 V; < 0,01%/cycle, up to 80% EE) developed for AORFB prototype

- Deeper understanding of structure-stability relation have been gained

- Scale-up process is a critical role in the irruption of new chemistries

- Chemistry and electrolyte impacts battery at all the stages: construction, operation, maintenance and end of life

- Even if electrolyte is set as core of the development of new technologies a joint development is needed to consider all stages to prototype

Thank you!

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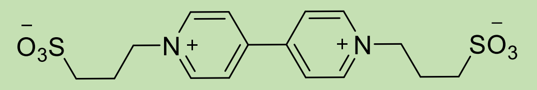
Disclaimer/ Acknowledgment

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 875613. The information and views set out in this publication does not necessarily reflect the official opinion of the European Commission. Neither the European Union institutions and bodies nor any person acting on their behalf, may be held responsible for the use which may be made of the information contained therein.

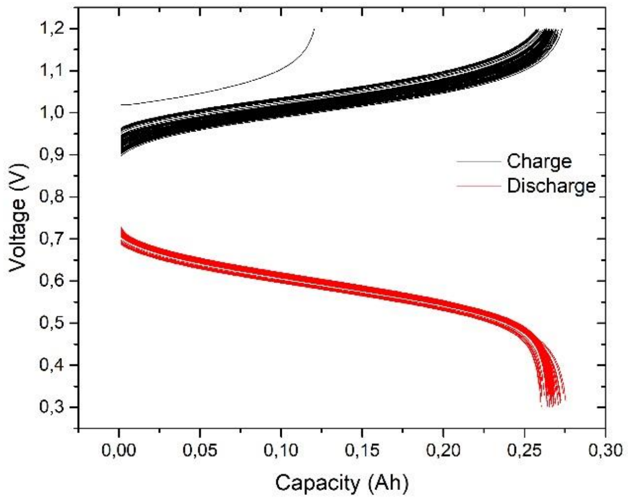


Electrolyte formulation – Starting point

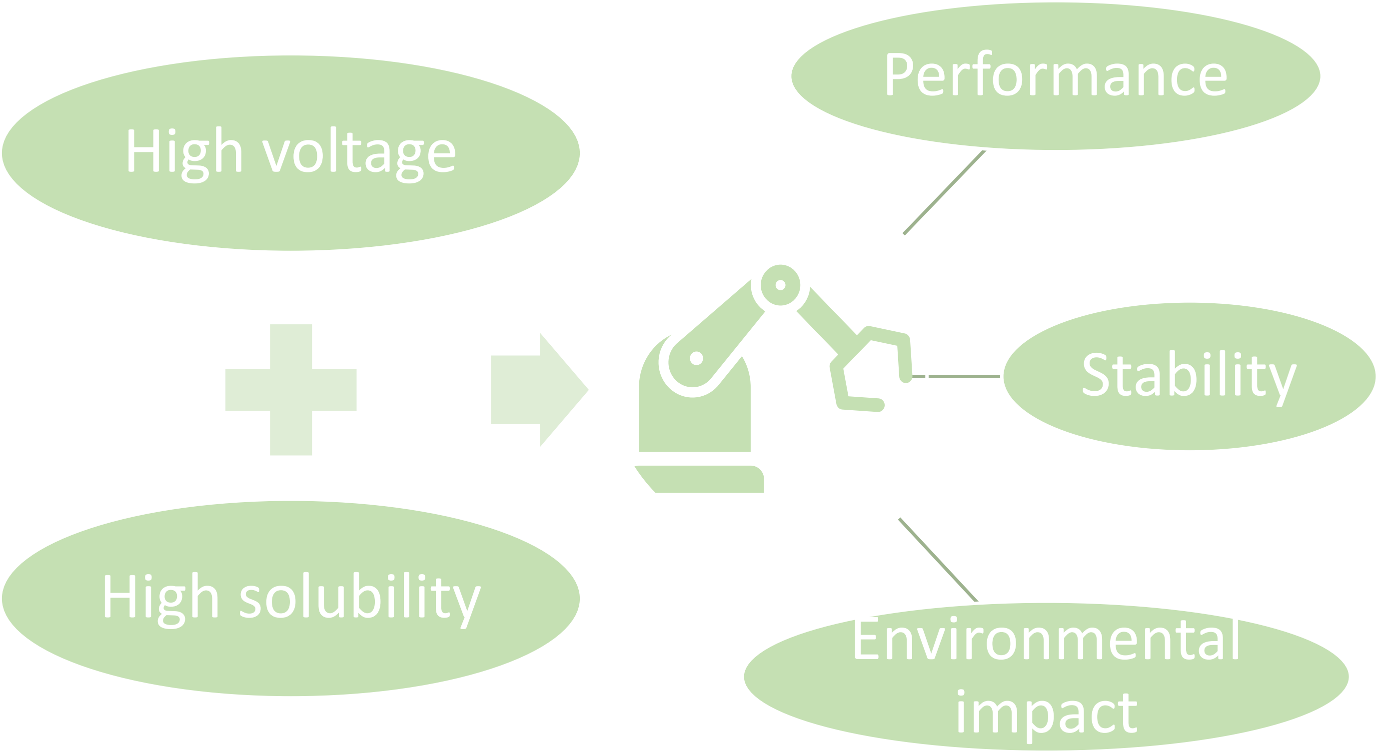
- **Active materials are main but not only component of electrolytes**
  - pH, supporting electrolyte salts, charge carriers
  - Temperature, SoC & operating conditions

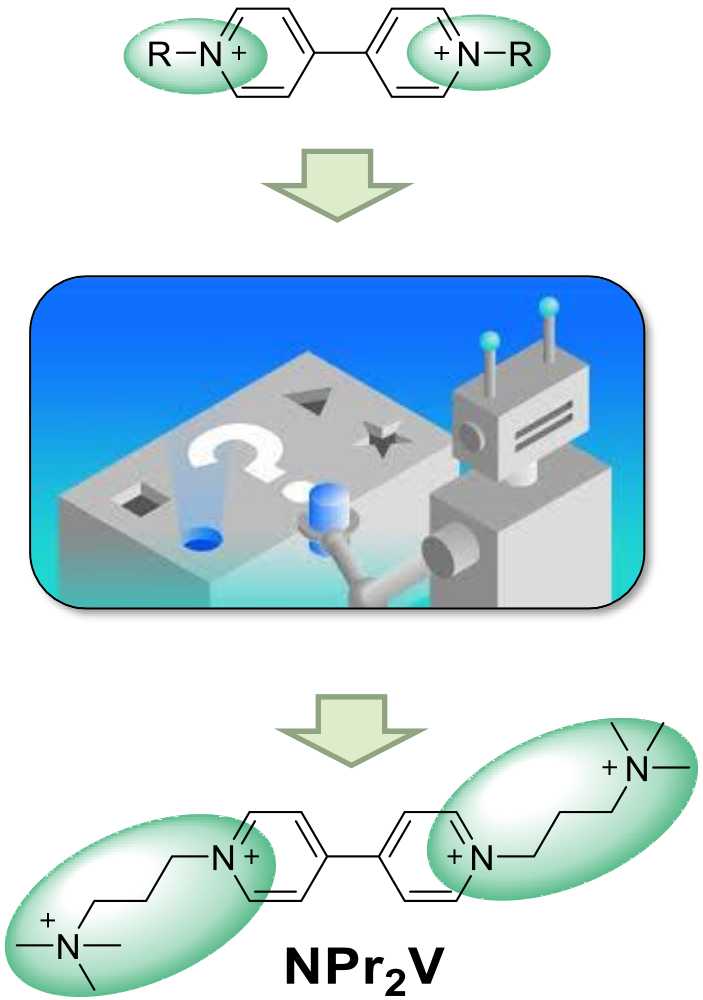
Active Material (M)	Supp. Electrolyte (M)	σ (mS cm^{-1}) (25°C)	η (cP) (25°C)
B2-2 (0.9M)	NH_4Cl (1.0M)	51	3.2
B2-2 red (0.9M)	NH_4Cl (1.0M)	78	4.5
B2-2 (0.9M)	NH_4Cl (1.5M)	62	3.2
B2-2 (0.9M)	NH_4Cl (2.0M)	79	3.2
B2-2 (0.9M)	NH_4Cl (3.0M)	110	3.5
C3-1 (0.9M)	NH_4Cl (1.0M)	324	1.4

- **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 $(NH4)_xM_{4-x}[Fe(CN)6]$ 0-45ºC
    - Conductivity and efficiency
    - Crossover: water transport depends on SoC/Ionic strength/T



New design


High voltage
High solubility
Performance
Stability
Environmental impact


R–N+
+N–R
NPr2V