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Electrical Energy Storage in Organic Redox-Flow Batteries

Thomas Turek
Institute of Chemical and Electrochemical Process Engineering, TU Clausthal

René Wilhelm
Institute of Organic Chemistry, TU Clausthal

CCCE Clausthal Conference on Circular Economy
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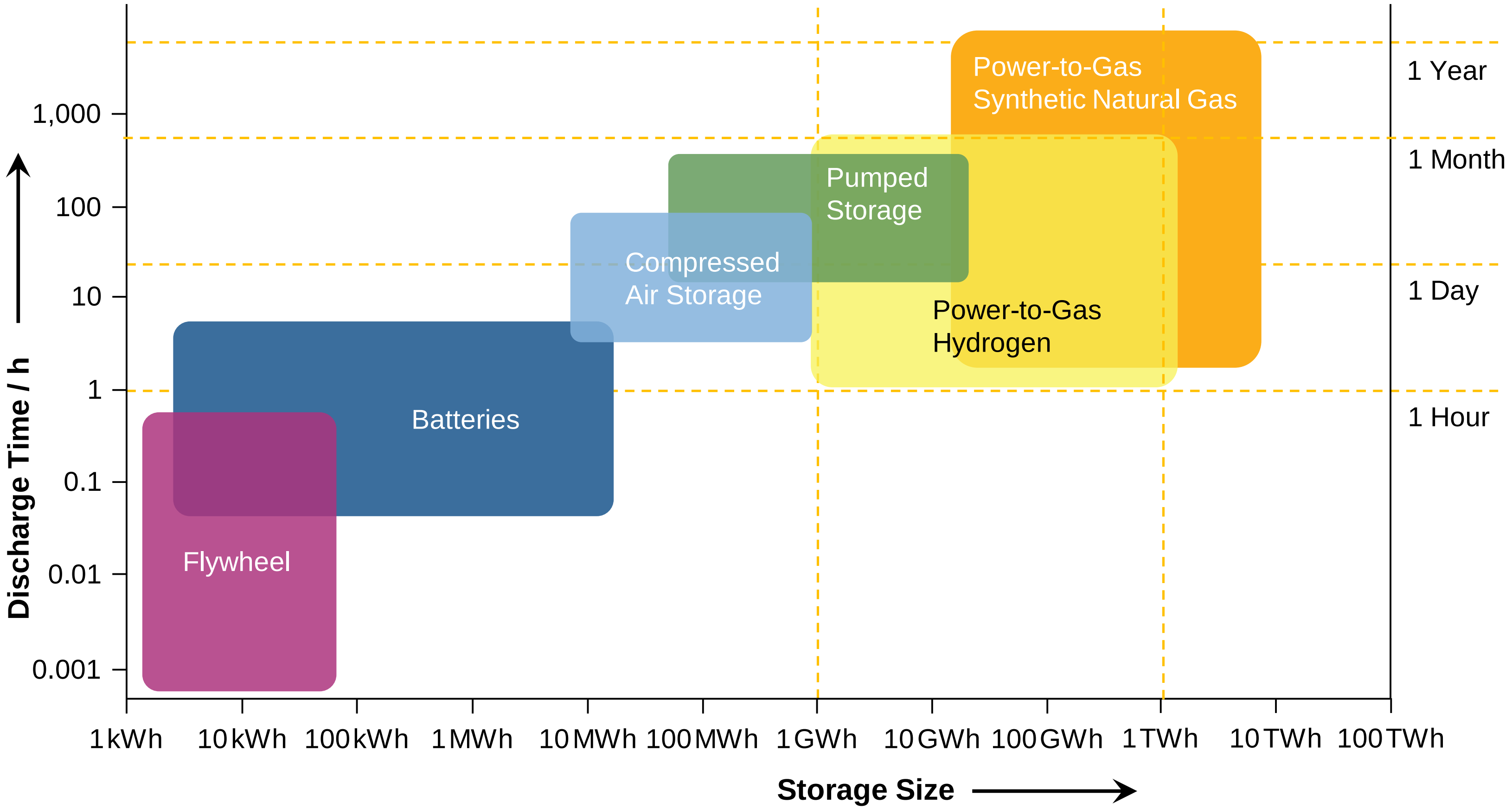
Selected Energy Storage Systems



Adapted from ltm-power.com

Many Different Types of Batteries

Primary batteries

- Not rechargeable
- Alkali-manganese, Zinc-air, …

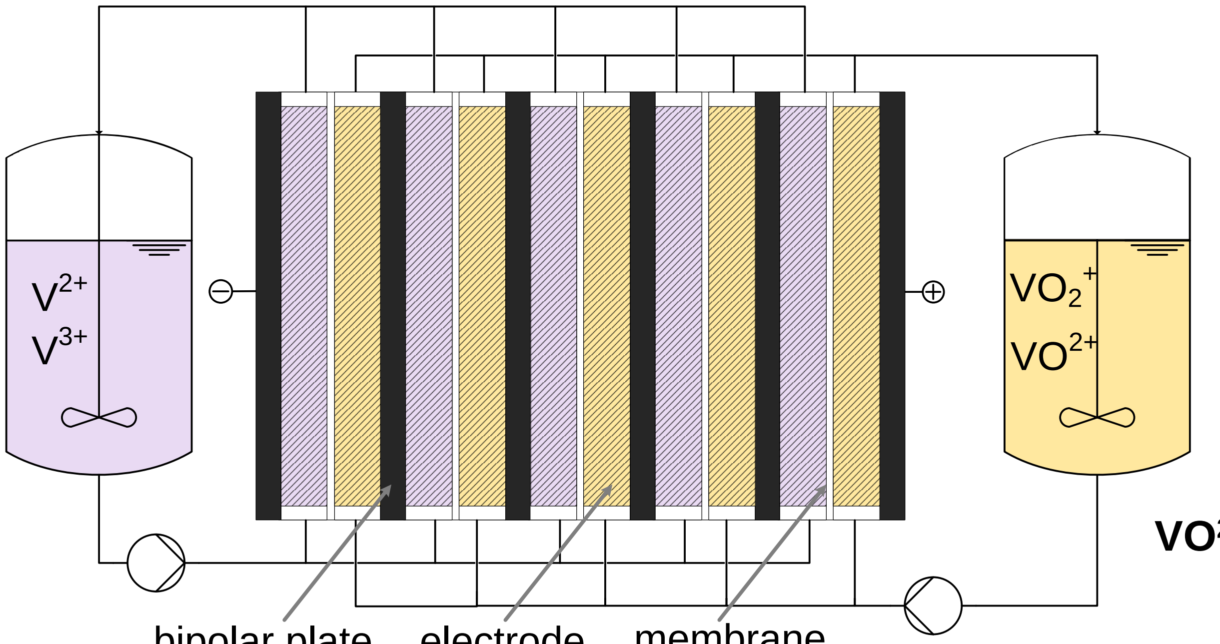
Secondary batteries

- Rechargeable
- Li-ion, Lead-acid, …

Redox-flow batteries (RFB)

- Flowing electrolyte
- Tanks for energy storage
- Cells for charge/discharge

“All Vanadium” Redox-Flow Battery (RFB)



negative electrolyte (NE)

$V^{2+} \leftrightarrow V^{3+} + e^-$

positive electrolyte (PE)

$VO^{2+} + H_2O \leftrightarrow VO_2^+ + 2\,H^+ + e^-$

- Acidic electrolyte (1 - 2 M vanadium, 4 - 5 M sulfuric acid)
- Approx. 25 kWh/m³ energy density and 1 kW/m² power density
- Only for stationary storage, but intrinsically safe!

Components of RFB Cells

Bipolar plate

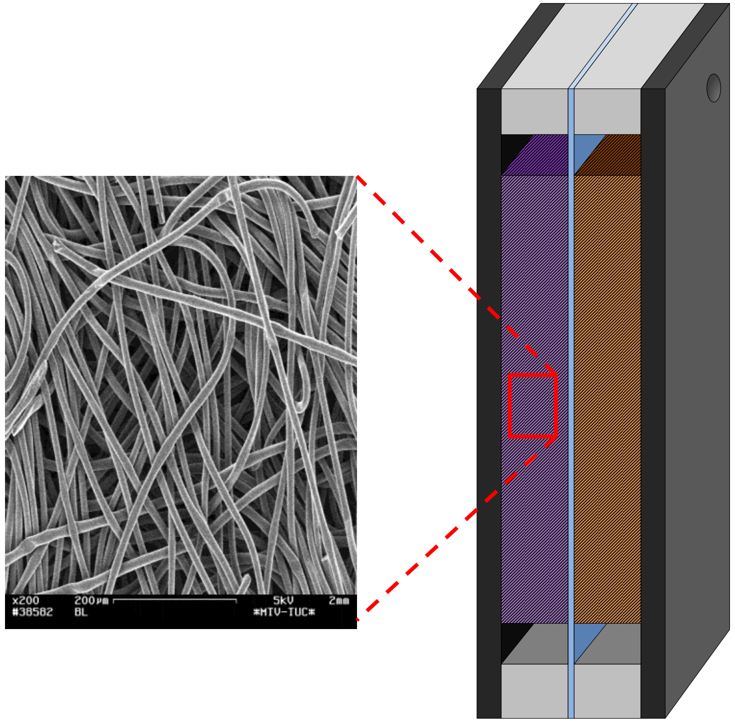
- Current collector
- Separates cells

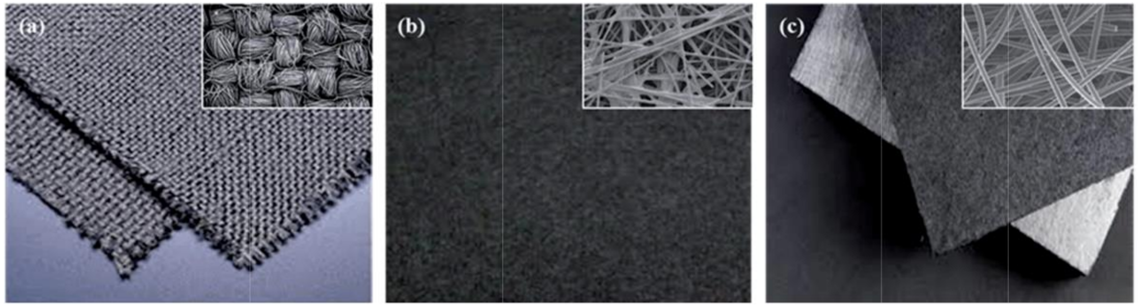
Ion-exchange membrane

- Prevents PE and NE from mixing
- Charge balance

Carbon felt electrodes

- High porosity → permeable for electrolyte
- NE: $V^{2+} \leftrightarrow V^{3+} + e^-$
- PE: $VO^{2+} + H_2O \leftrightarrow VO_2^+ + 2\ H^+ + e^-$





K.J. Kim, M.-S. Park, Y.-J. Kim, J.H. Kim, S.X. Dou, M. Skyllas-Kazacos, J Mater Chem A 3 (2015) 16913

Commercial RFB Battery Systems

Home storage systems

- Voltstorage, Volterion, …
- Typical values 1,5 kW power, 6,8 kWh energy content

Industrial storage systems

- Sumitomo (Japan), Cellcube (Austria), …
- Solar and wind parks
- Up to several MWh energy content and MW power
- Lifetime up to 20 years demonstrated

Photos: Voltstorage.com, Sumitomo.com

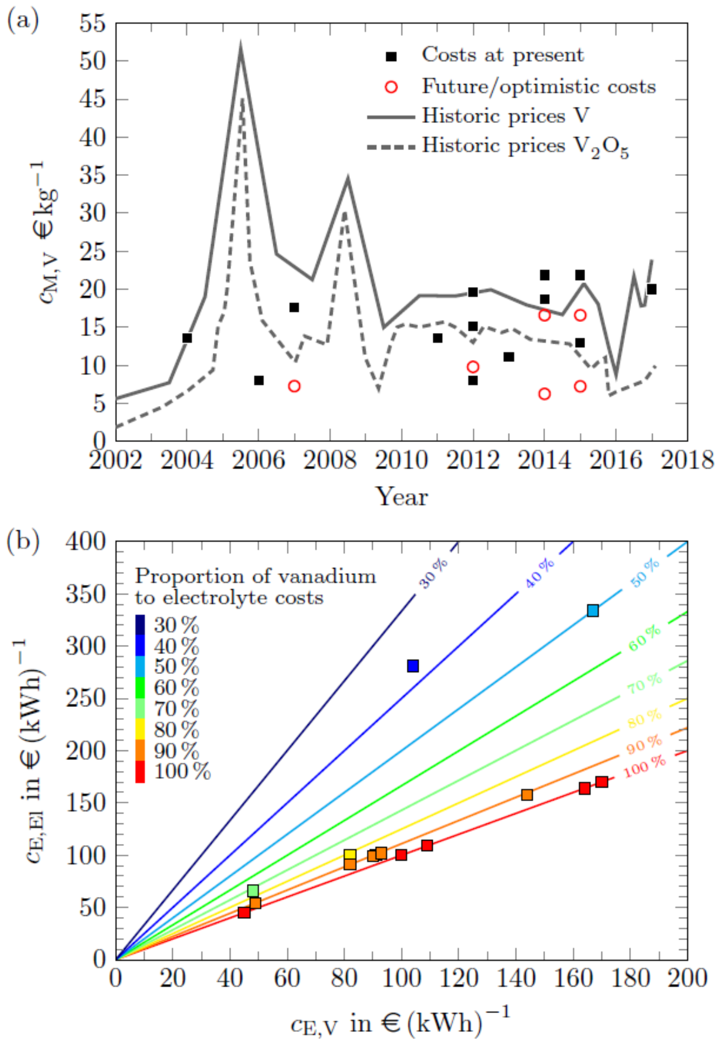
The Vanadium Problem

Price development

- Strongly fluctuating and relatively high
- Dependent on use in steel industry
- Vanadium = critical raw material!

Breakdown of system costs

- Cost drivers electrolyte, membrane, bipolar plate
- Approx. 50% contribution of Vanadium to total costs!
- In many cases not competitive with Li-ion battery



C. Minke, T. Turek, J Power Sources 376 (2018) 66-81

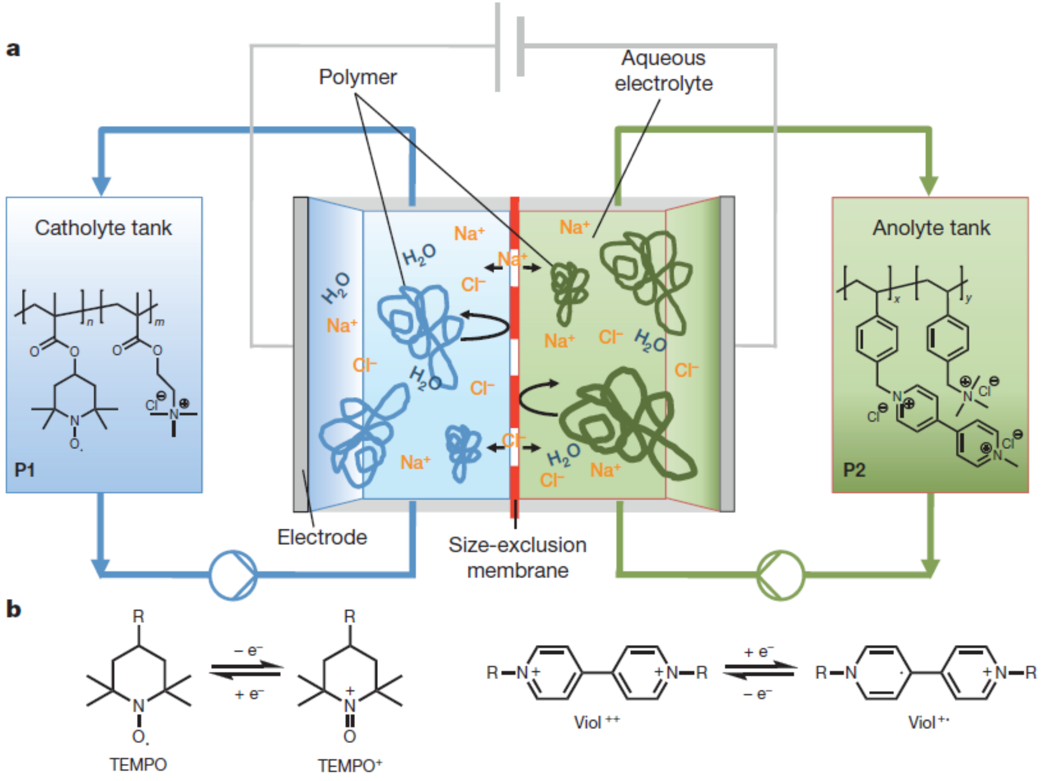
New Development: Organic RFB

Possible advantages

- Abundant renewable raw materials could be used
- Possibly cheaper than Vanadium
- Larger molecules result in lower cross-over thorough membrane

Challenges

- Long-term stability (temperature, electrochemical stress, contact with air)
- High solubility and low viscosity required
- “Exotic” molecules could be too expensive

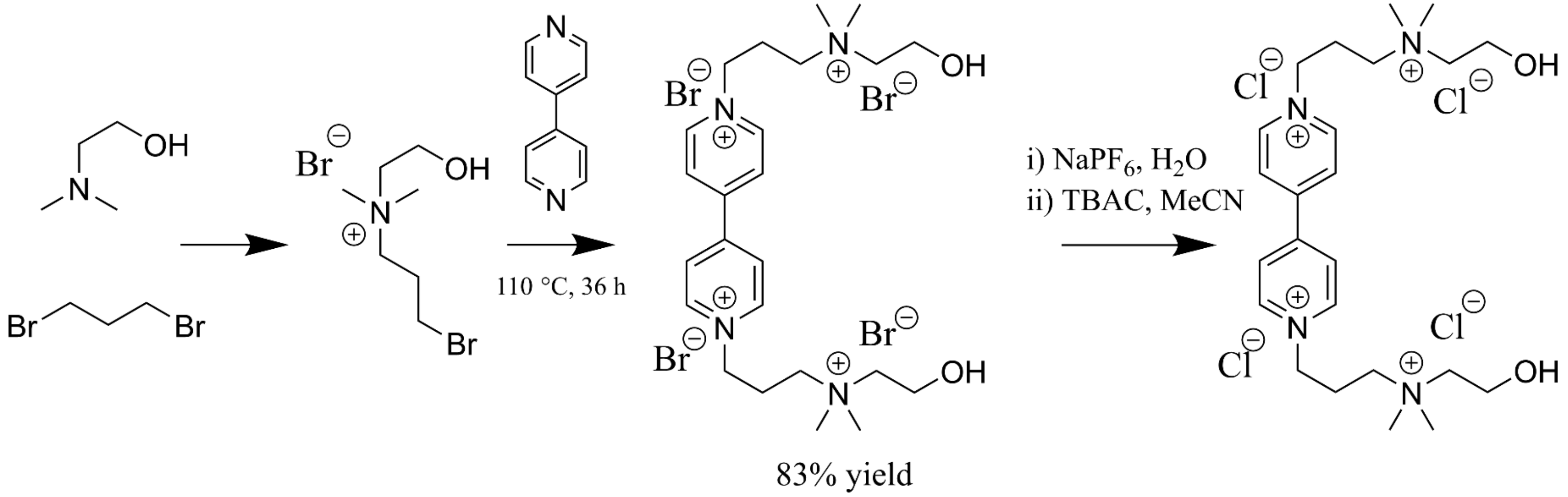


U. S. Schubert et al., Nature 527 (2015) 78

Hydroxylated Tetracationic Viologen

New Negolyte

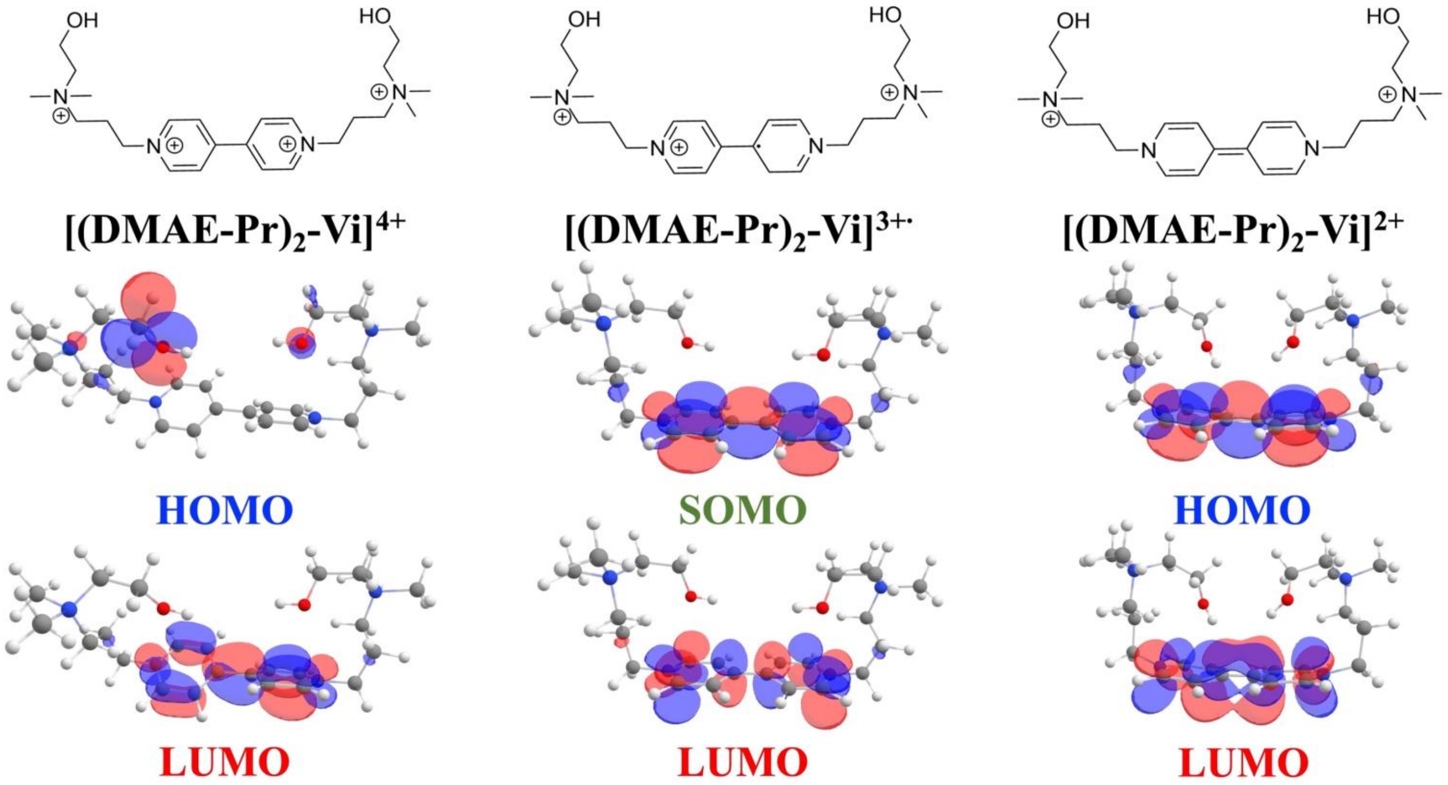
- Permanently charged moiety, switching from the trimethylammonium group to a dimethylaminoethanol (DMAE) derivative, max. 2.7 M in water, D = $3.92 \cdot 10^{-6}$ $cm^2 s^{-1}$



[(DMAE-Pr)$_2$-Vi]Cl_4

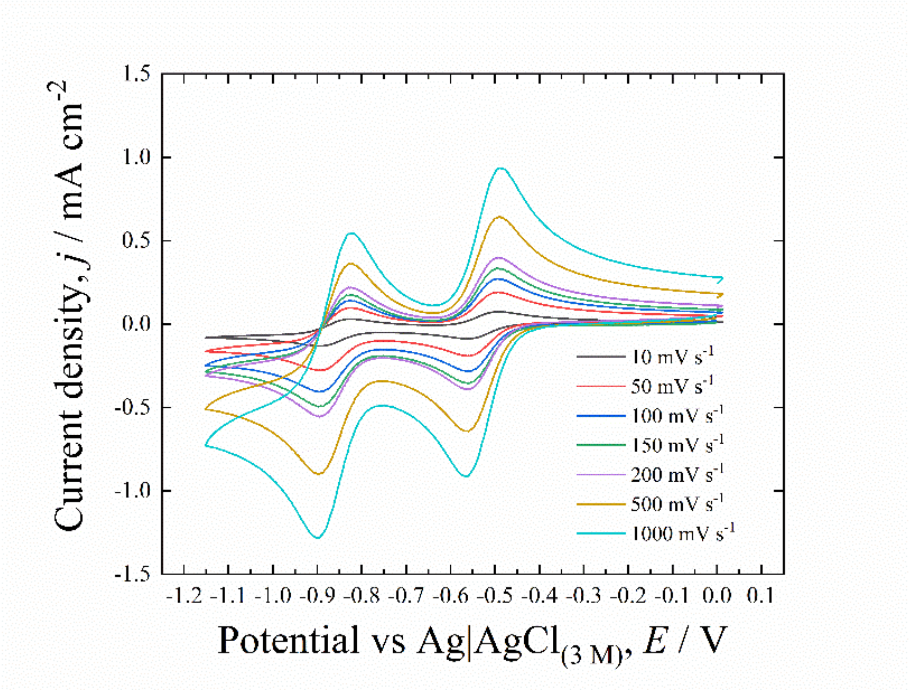
DFT Calculation of the Negolyte in Water

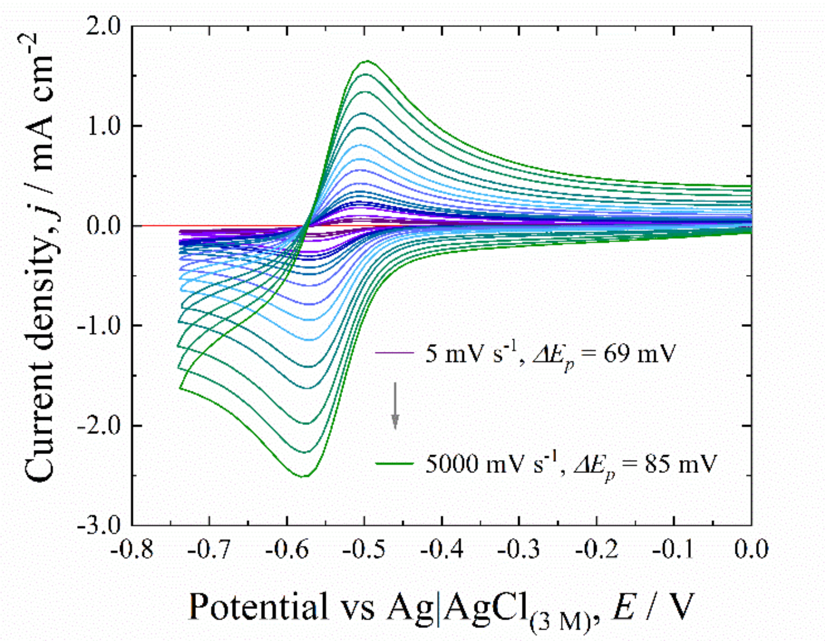
- Oxygen atoms of the OH-groups always point at the redox centers (i.e., the bipyridinium rings) of $[(DMAE\text{-}Pr)_2\text{-}Vi]^{4+}$ and $[(DMAE\text{-}Pr)_2\text{-}Vi]^{3+}$
- Dihedral angle between ring in the cationic radical is 4.83
- This can explain observed stability of the 1st reduced species compared to other viologen analogues where dimerization can be a problem



CV of Hydroxylated Tetracationic Viologen

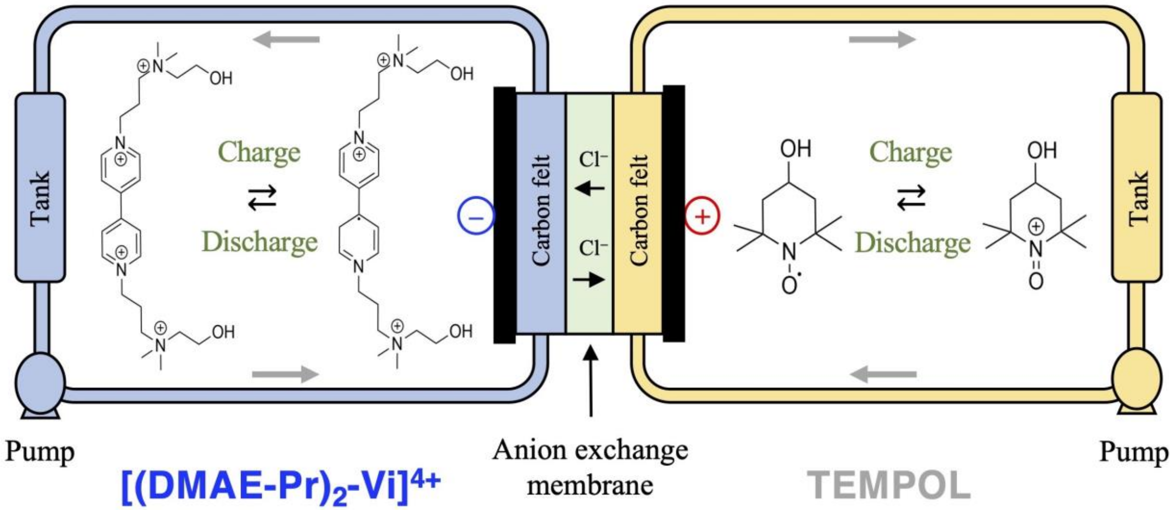
- Cyclic voltammetry at low concentration shows two redox events at –0.53 V and –0.89 V (vs Ag/AgCl) respectively.
- Remarkable reversibility was found for the first reduction (Δpeak= 85 mV at 5 V s^{-1}).

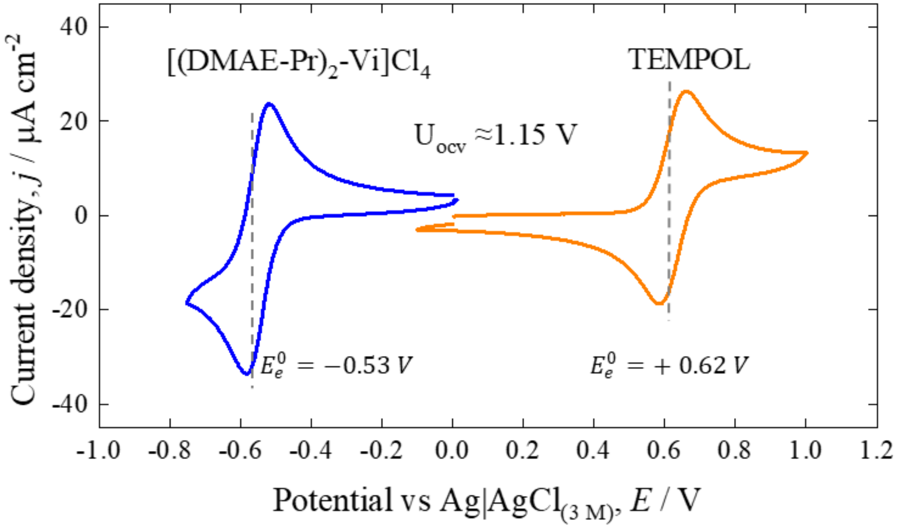




New Negolyte for a Neutral Aqueous Flow Battery

- 1 M KCl chosen as the supporting electrolyte while the concentration of the redox active species was 0.1 M
- Low-cost anion exchange membrane - FAS-30 (30 µm) - proved to be a feasible alternative to the commonly used Selemion DSVN



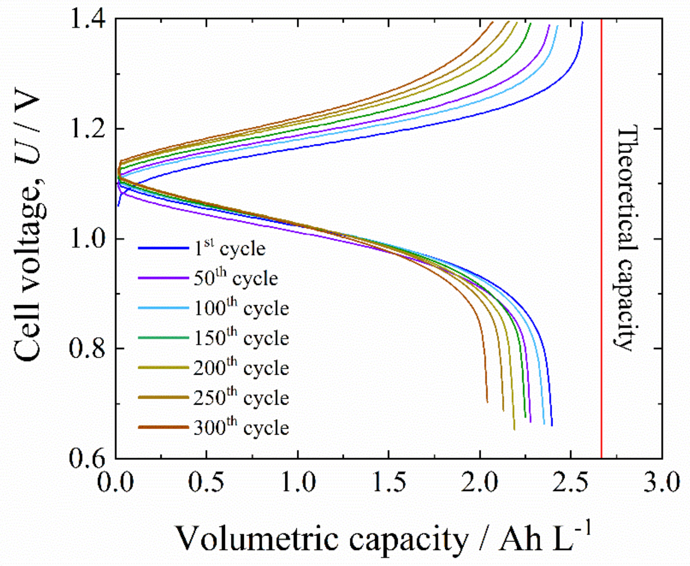


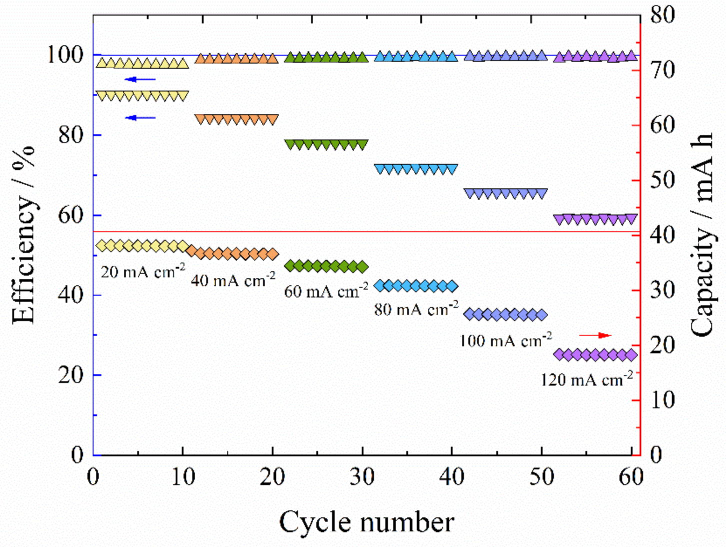
Experimental Setup

- 4 cm^2 cell (carbon felt)
- Viton, N_2 supply, sealed tanks, FEP tubing, etc.
- Flow rate: ≈ 1 $cm\ s^{-1}$
- 40 $mA\ cm^{-2}$

Cell Performance

- Maximum accessible capacity 94 % at 20 mA cm^{-2}
- Coulomb efficiency above 98 %, while Energy efficiency ranged from 57 to 90 %
- Long galvanostatic charging-discharging test was performed at 40 mA cm^{-2}
- Cell sustained 300 cycles, for a total of 127 h of operation
- Calendar fade rate was 3.1 % per day (or 0.05 % per cycle)
- Post-mortem CV analysis revealed severe cross-over of TEMPOL

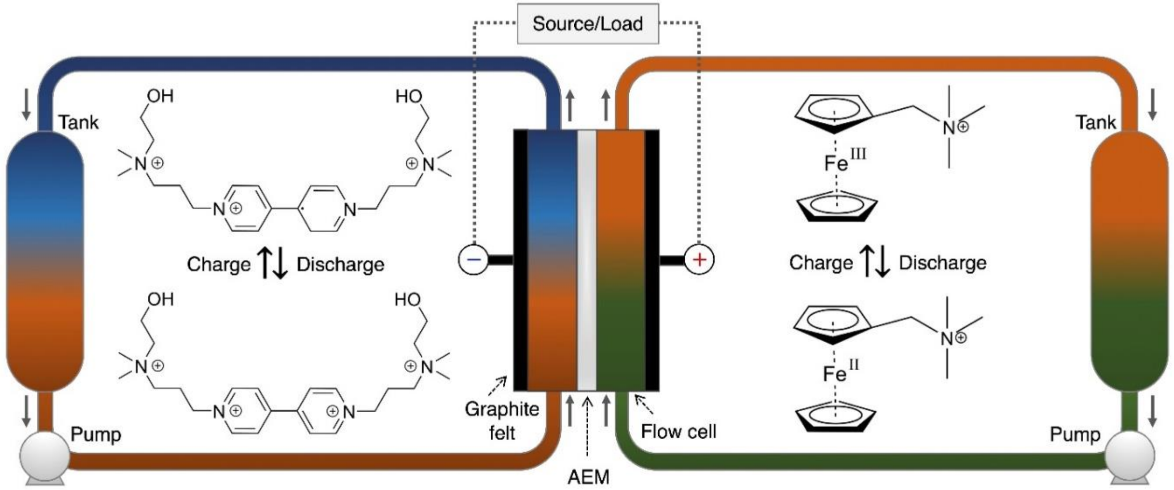


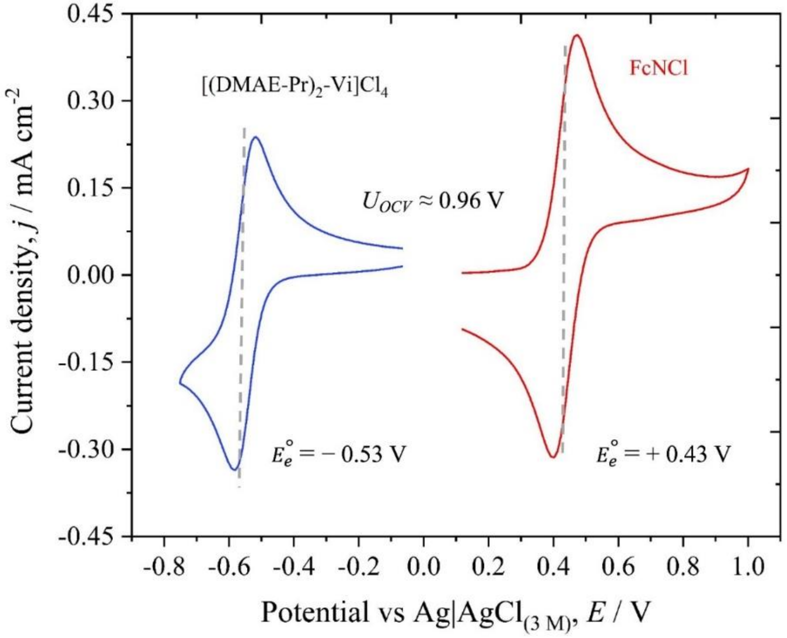


C. Caianiello, L. F. Arenas, T. Turek, R. Wilhelm, Batt. Supercaps 6 (2023) e202200355

Replacing TEMPOL with FcNCl in the Flow Battery

- 1 M KCl chosen as the supporting electrolyte while the concentration of the redox active species was 0.1 M
- Low-cost anion exchange membrane - FAS-30 (30 μm) - proved to be a feasible alternative to the commonly used Selemion DSVN

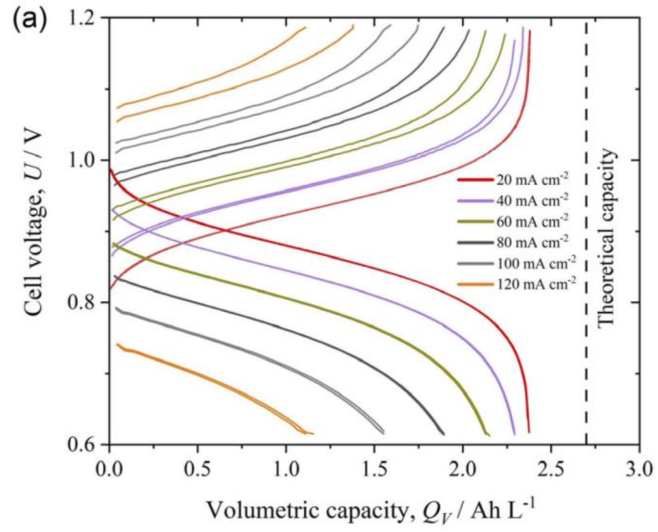


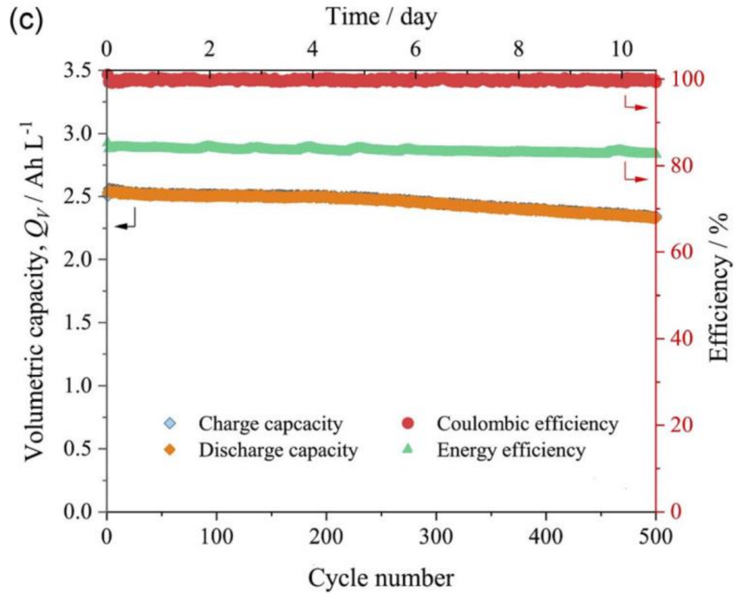


Cell Performance – with FcNCl

- Maximum accessible capacity 90 % at 20 mA cm^{-2}
- Coulomb efficiency above 99 %, while Energy efficiency ranged from 60 to 91.6 %
- Long galvanostatic charging-discharging test was performed at 40 mA cm^{-2}
- Cell sustained 500 cycles, for a total of 265 h of operation
- Calendar fade rate was 1 % per day (or 0.02 % per cycle)
- Post-mortem CV and NMR analysis revealed small cross-over of FcNCl

C. Caianiello, L. F. Arenas, T. Turek, R. Wilhelm, Adv. Energy Sustainability Res. Express 10 (2023) 075501





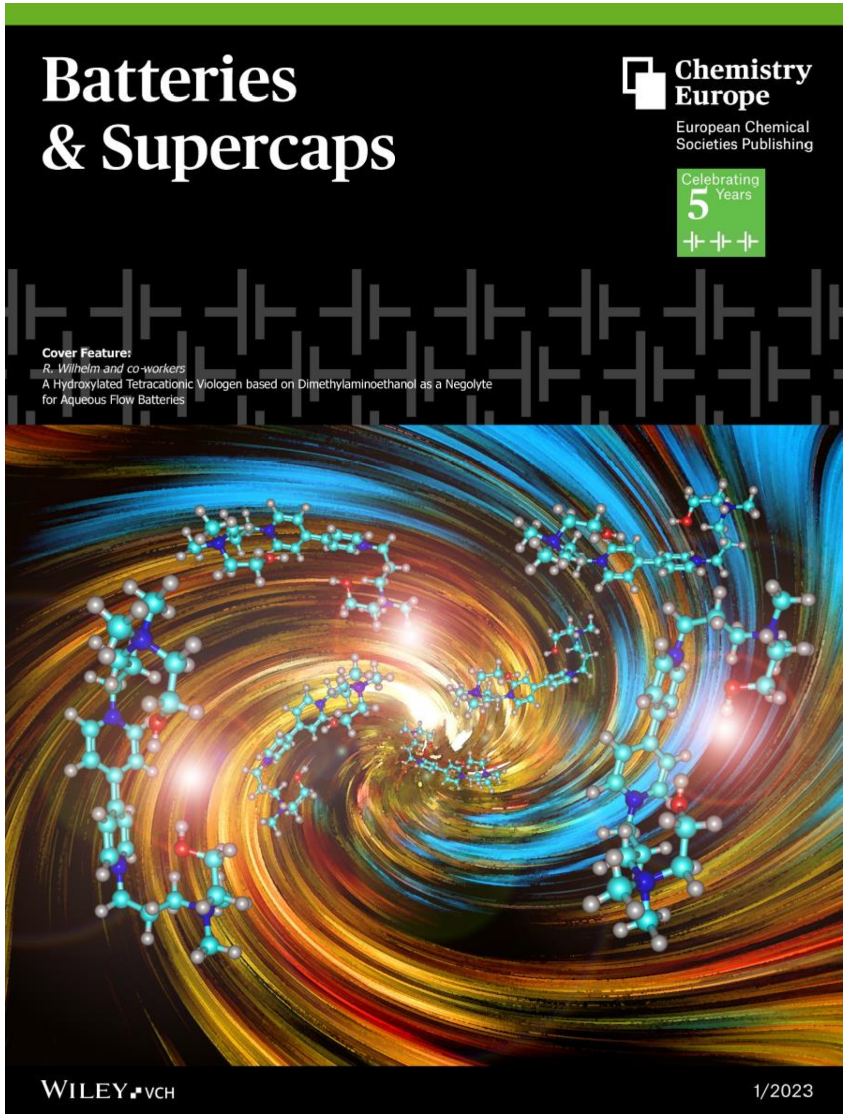
Summary and Outlook

Flow batteries

- Interesting alternative battery systems
- Intrinsically safe
- Suitable for stationary storage

Organic electrolytes

- Rapid development during the last 10 years
- No critical raw materials required
- Proper choice of membrane materials
- Further work needed: performance, long-term stability



R. Wilhelm et al., Batt. Supercaps 6 (2023) e202200540

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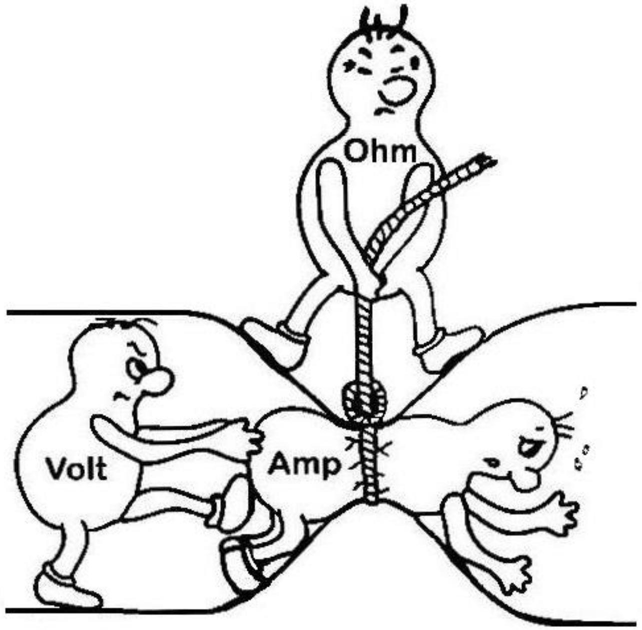







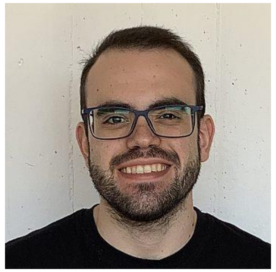


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