The importance of the electrolyte-membrane combination for long lifetime Viologen-Tempo AORFB

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Laura Pastor Muñoz

Eduardo Sánchez, Maddalen Agirre, Nerea Marquinez, Aitor Beloki

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Universidad del País Vasco
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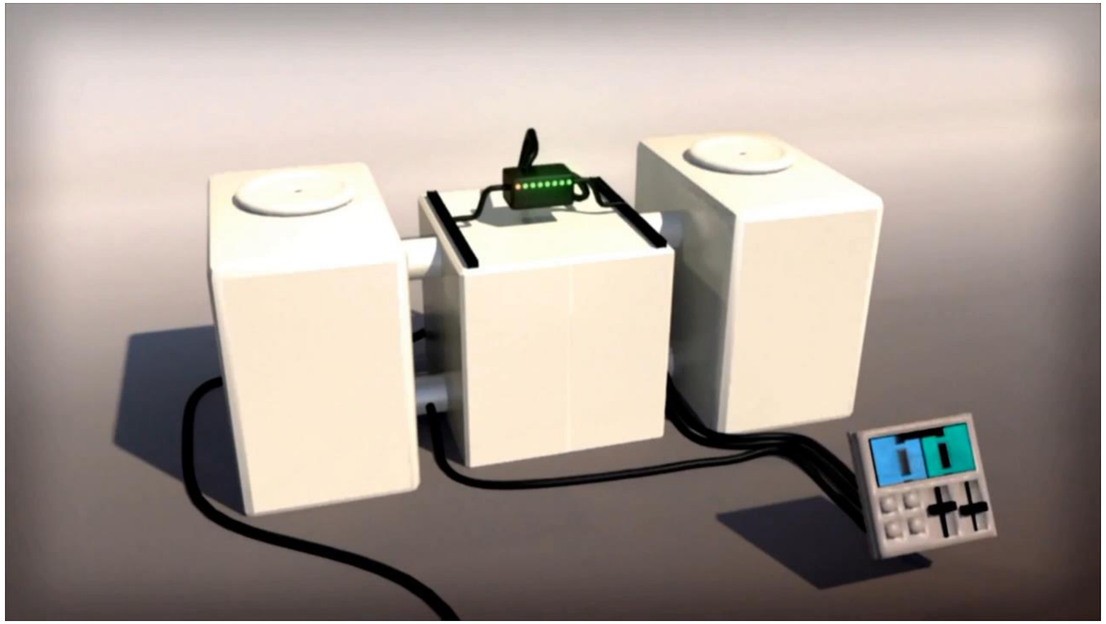
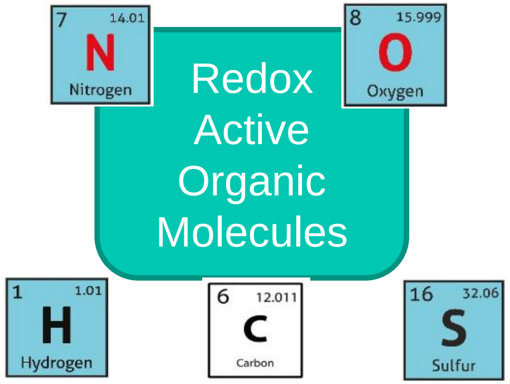
AORFB

GOING ORGANIC!



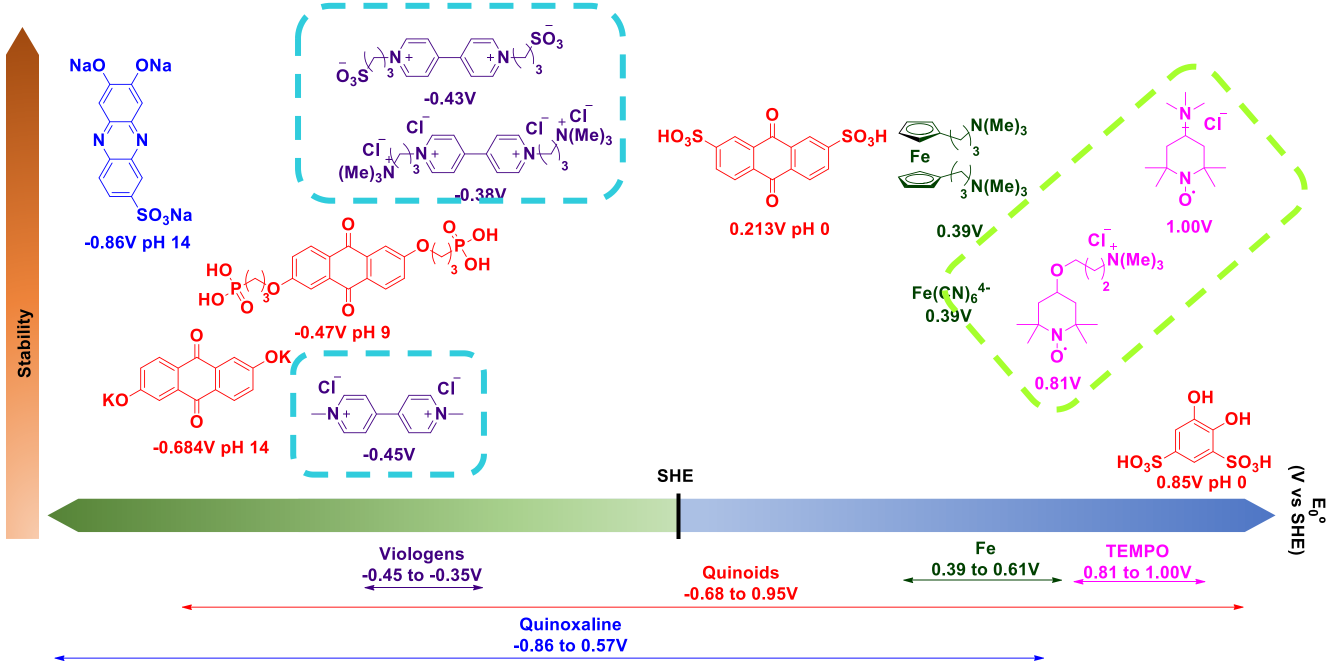
Aqueous
Organic
Redox
Flow
Batteries



- Earth abundant
- Low cost
- Environmentally friendly
- Thermally stable
- Easy tailorability

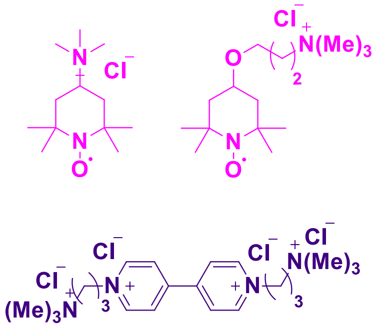
AORFB

SCOPE AND OBJECTIVE



Viologen-TEMPO (neutral pH)

- High solubility
- Rapid charge transfer kinetics
- High cell voltage



Synthesis: 2-3 steps
Complex Purification

Poor solubility in supporting electrolyte

Low efficiencies < 70%

Peak power densities < 100 mW/cm^2

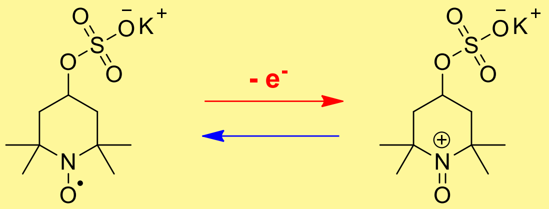
$(SPr)_2V$ – TEMPO-SO_4K
Cation Exchange membrane

AORFB: Viologen-TEMPO system

HIGH PERFORMANCE & LOW-COST SOLUTION

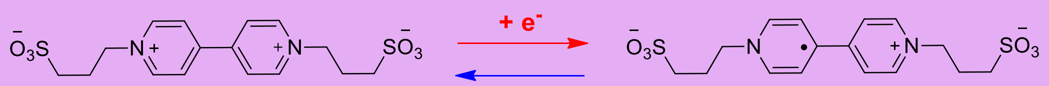
One-Step Straightforward Synthetic routes

Catholyte
TEMPO derivative



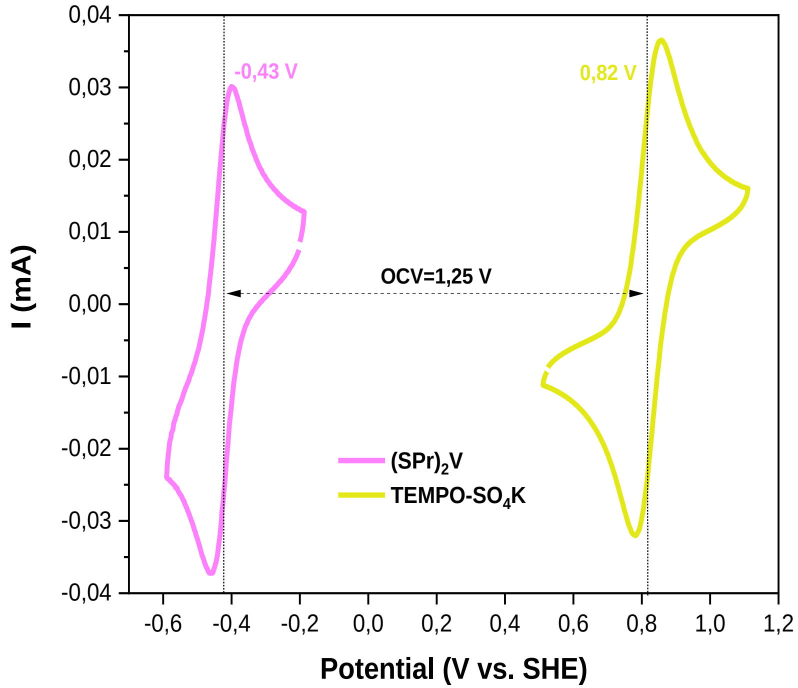
TEMPO-SO_4K

Anolyte
Viologen derivative



$(SPr)_2V$

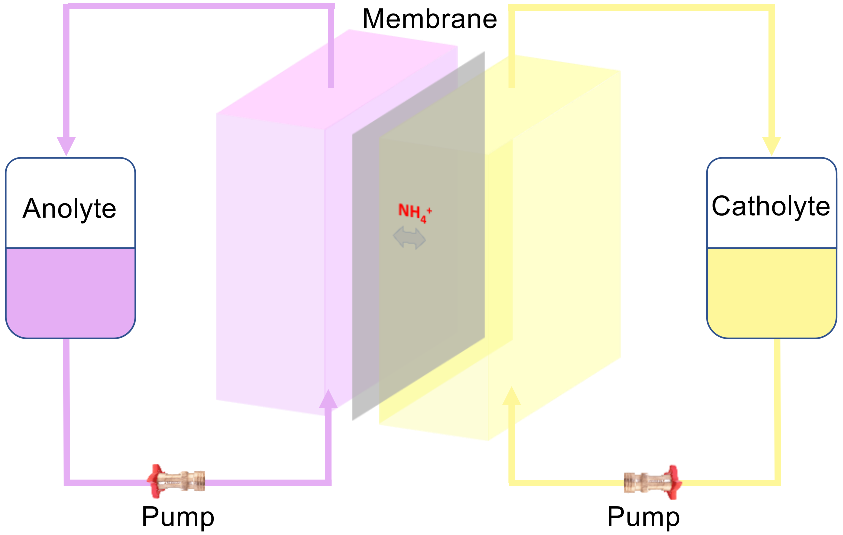
Joule 2019, 3, 1–15



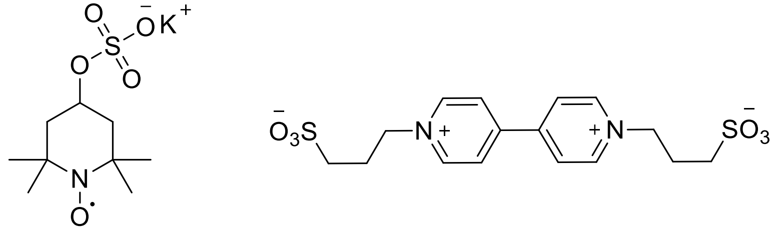
Electrochemical characterization and solubility

Compound	$E_{1/2}$ (V vs. SHE)	D ($cm^2\ s^{-1}$)	k_0 ($cm\ s^{-1}$)	Water solubility (M)
TEMPO-SO_4K	0,82	$8,9 \times 10^{-6}$	$1,5 \times 10^{-2}$	2,7
$(SPr)_2V$	-0,43	$2,0 \times 10^{-6}$	$2,6 \times 10^{-2}$	1,2

Electrolyte screening



Active material



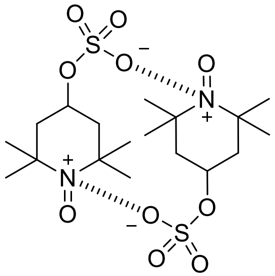
Supporting electrolyte

Low concentration trials

(N NaCl KCl NH_4Cl

High concentration of active material

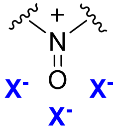
0.5 M Active material in 1 M KCl



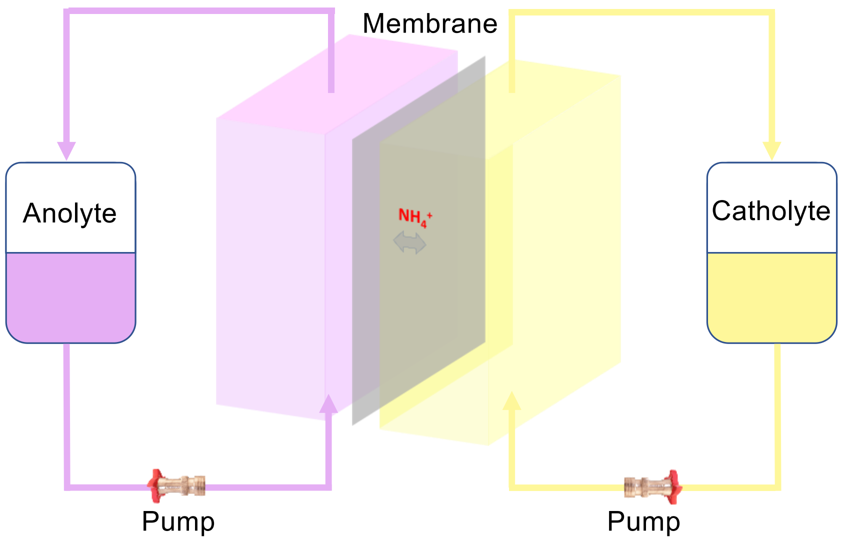
Large aggregates formation

Supporting electrolyte

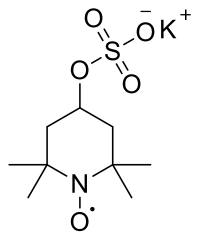
Anion shielding

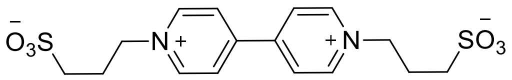


Electrolyte screening



Active material





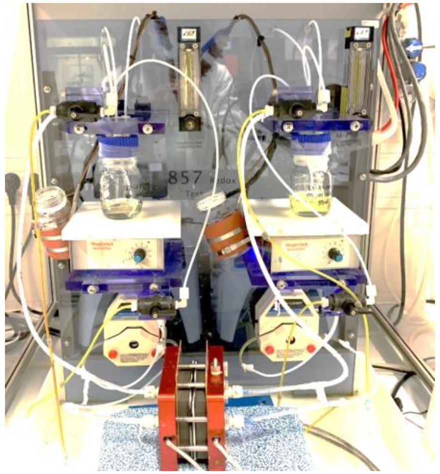
Supporting electrolyte $(NH_4)_2SO_4$ NaCl KCl NH_4Cl

	Anolyte	Catholyte	σ (mS/cm)	
A	0,5M SPr_2V + 2,6M **NH_4Cl**	0,5M TEMPO-SO_4K + 3,6M **NH_4Cl** + 0,9M **KCl**	186	271
B	0,5M SPr_2V + 2M **NaCl**	0,5M TEMPO-SO_4K + 3,5M **NaCl**	60	153
C	0,5M SPr_2V + 1,5M **$(NH_4)_2SO_4$**	0,5M TEMPO-SO_4K + 2M **$(NH_4)_2SO_4$**	91	175

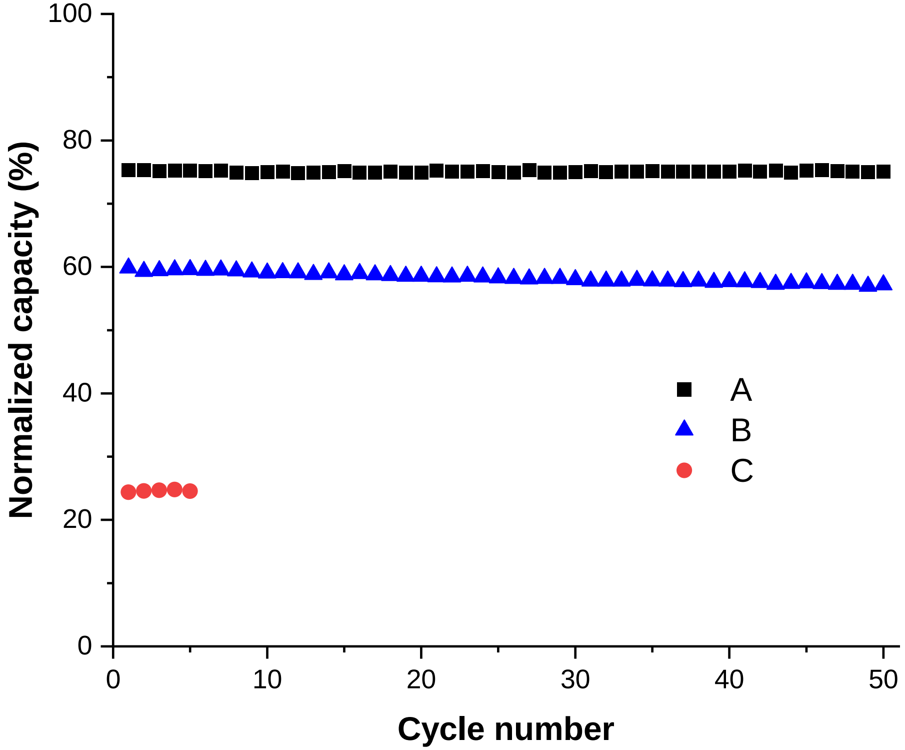
Electrolyte screening

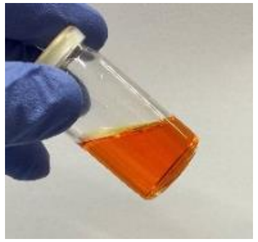
CELL TESTING

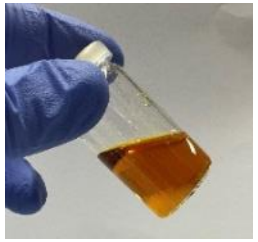
	Anolyte	Catholyte	R_{ohm} ($\Omega \cdot cm^2$) SOC 50
A	0,5M SPr_2V + 2,6M **NH_4Cl**	0,5M TEMPO-SO_4K + 3,6M **NH_4Cl** + 0,9M **KCl**	1,68
B	0,5M SPr_2V + 2M **NaCl**	0,5M TEMPO-SO_4K + 3,5M **NaCl**	2,26
C	0,5M SPr_2V + 1,5M **$(NH_4)_2SO_4$**	0,5M TEMPO-SO_4K + 2M **$(NH_4)_2SO_4$**	1,92

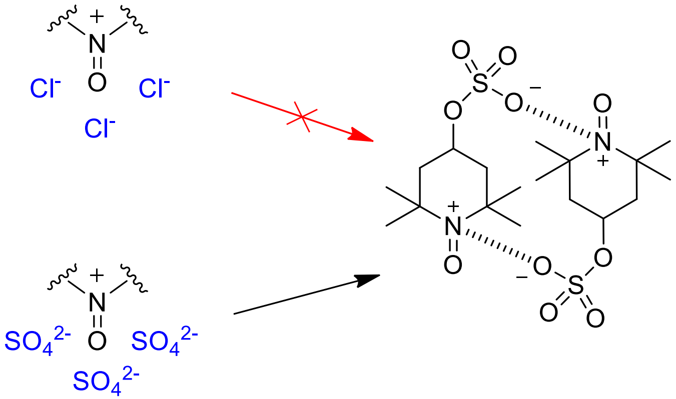


Membrane	FS950
Electrode	GFD 4,6EA
Cell area(cm^2):	25
Current (mA/cm^2):	60
Cut off voltage (V):	0,75-1,5



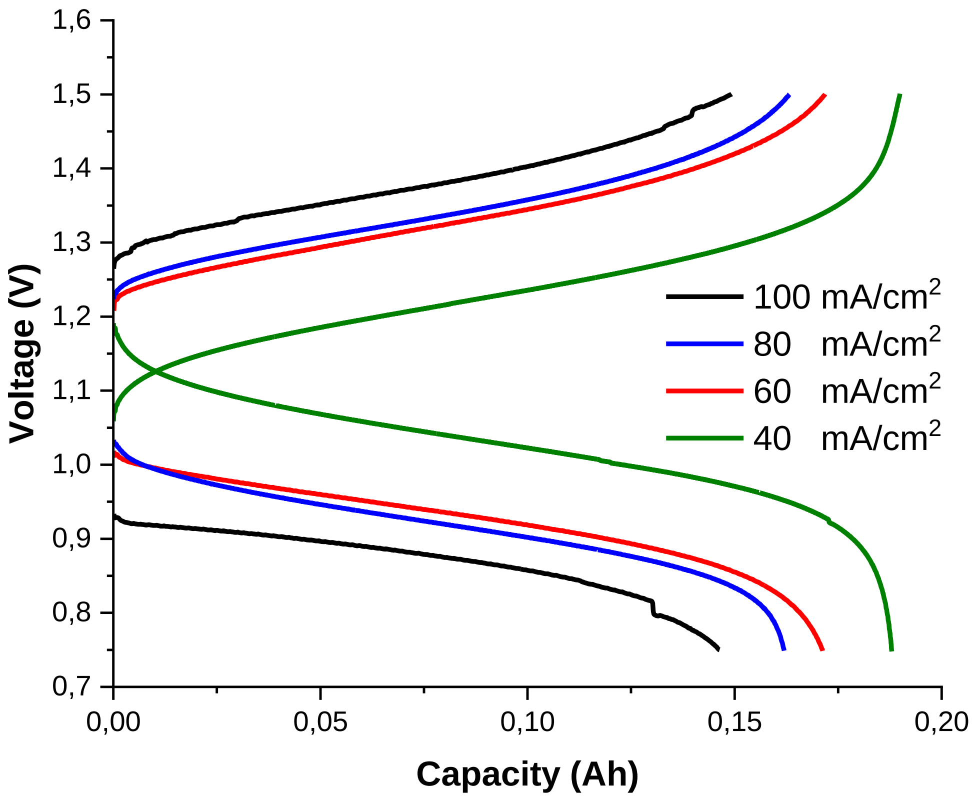


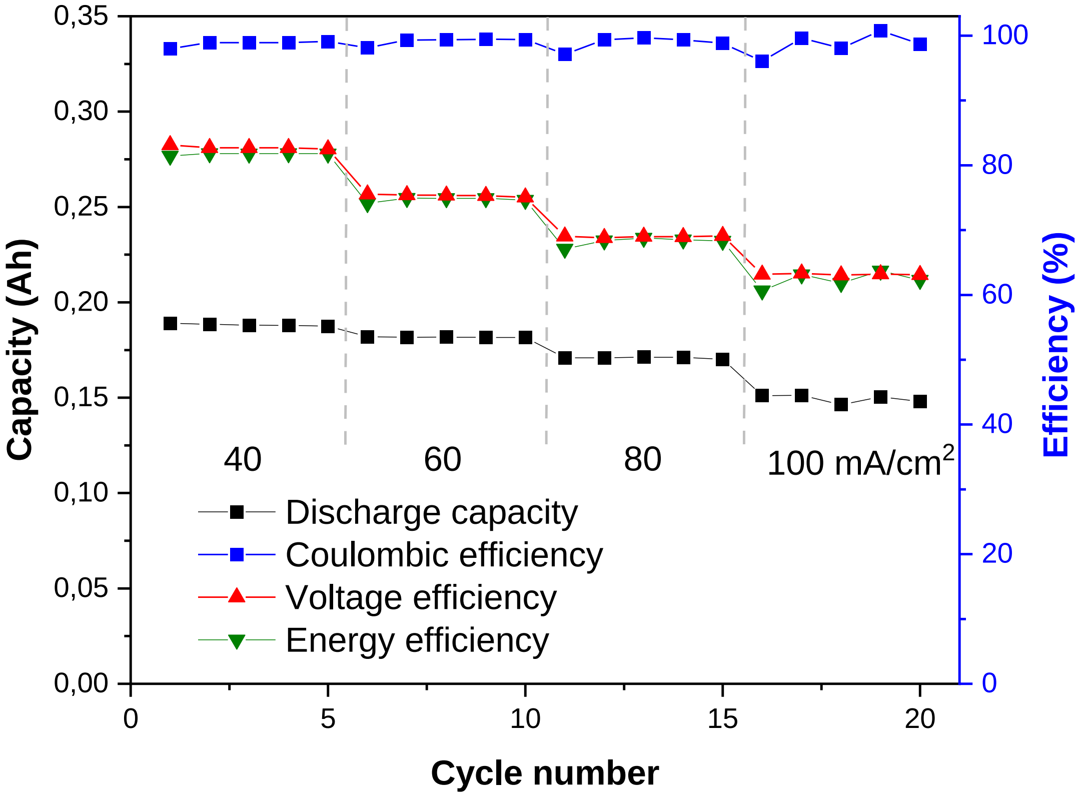




> Comparative study of membranes

Final electrolyte formulation
0,5M TEMPO-SO_4K in 3,6M NH_4Cl + 0,9M KCl
0,5M $(SPr)_2V$ in 2,6M NH_4Cl





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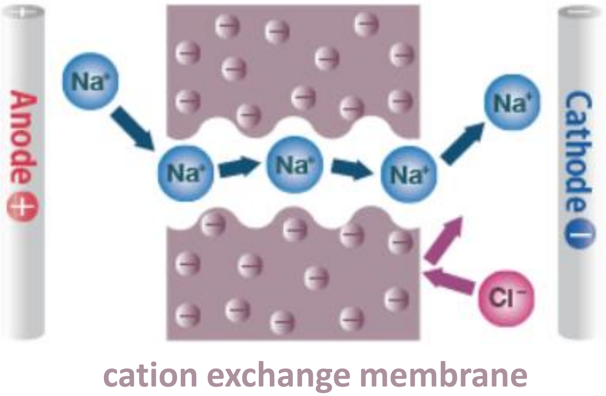


E87-05S

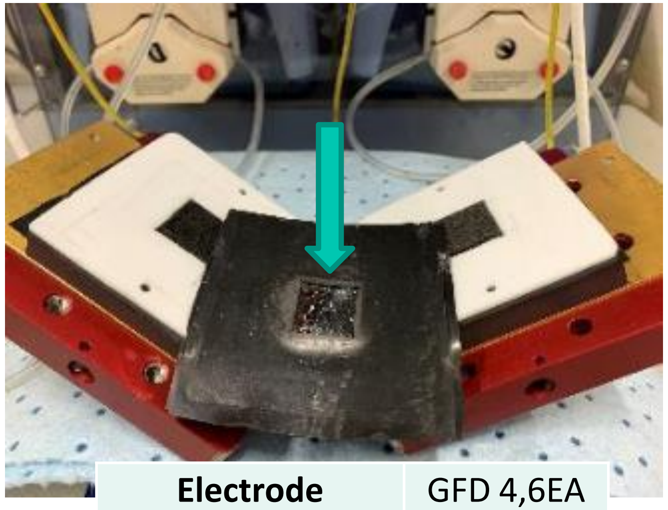
NR-212

SX-053WK

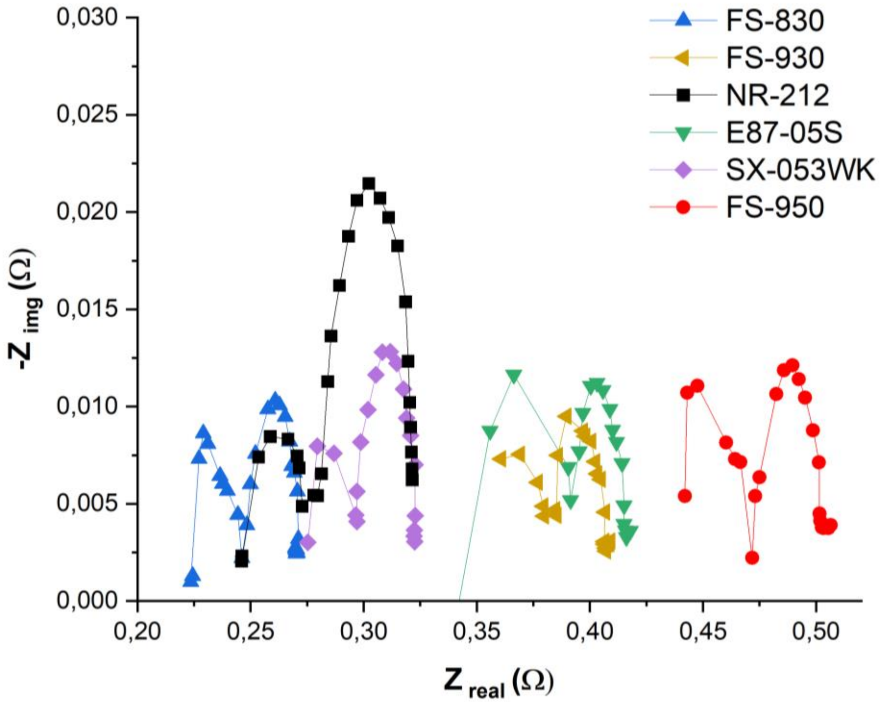
Fumasep membranes

FS-950 FS-830

FS-930



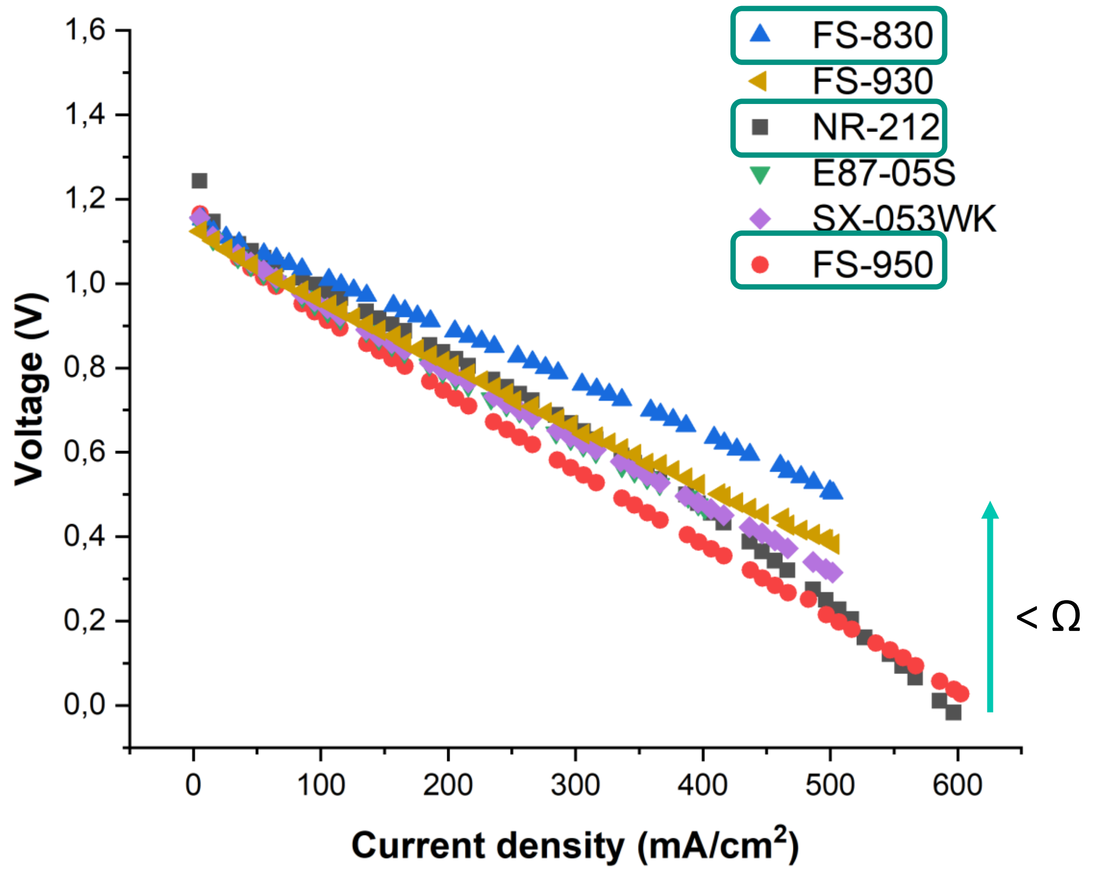
Electrode	GFD 4,6EA
Cell area(cm^2):	5
Flow (mL/min):	80
Cut off voltage (V):	0,75-1,5



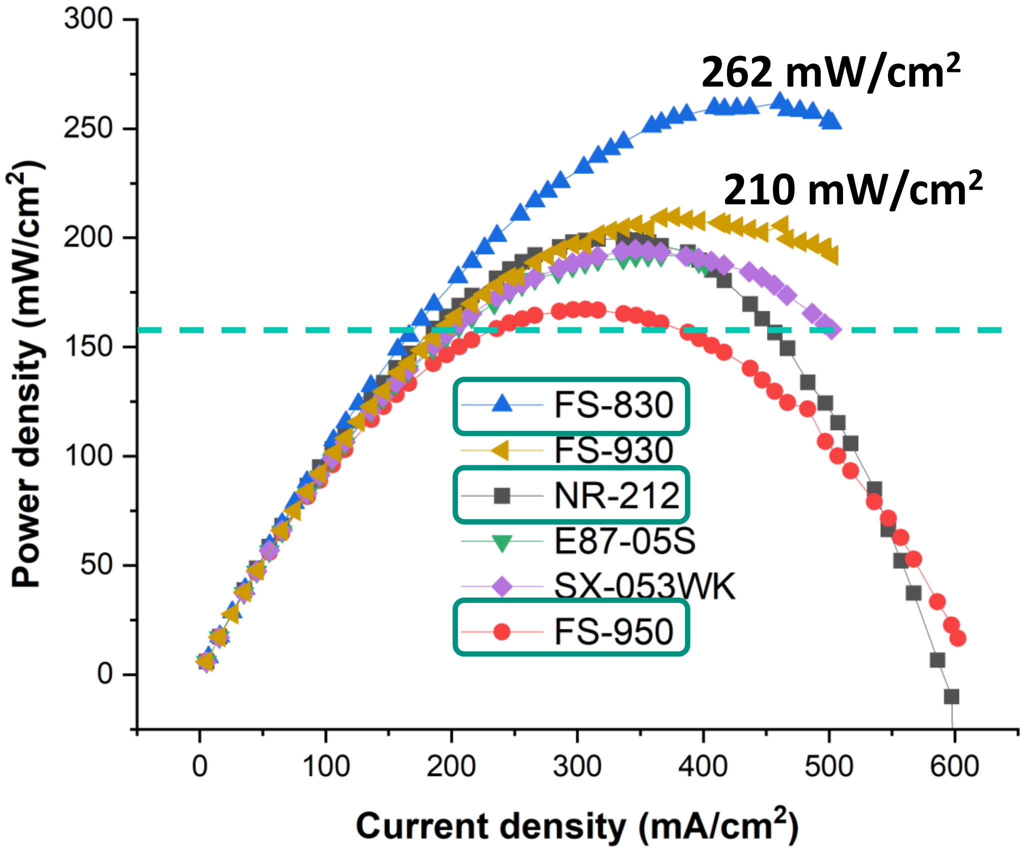
Comparative study of membranes

TRANSPORT PHENOMENA

Polarization Curves SOC 50

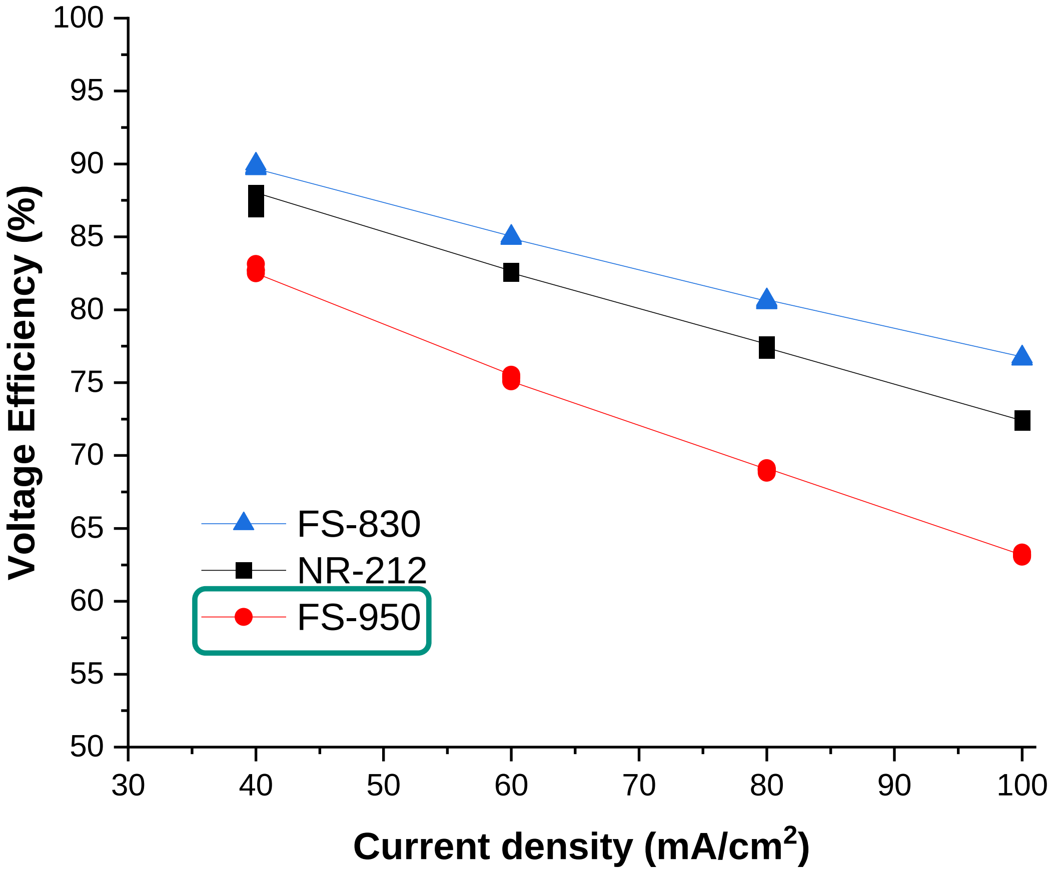


Power density curves SOC 50

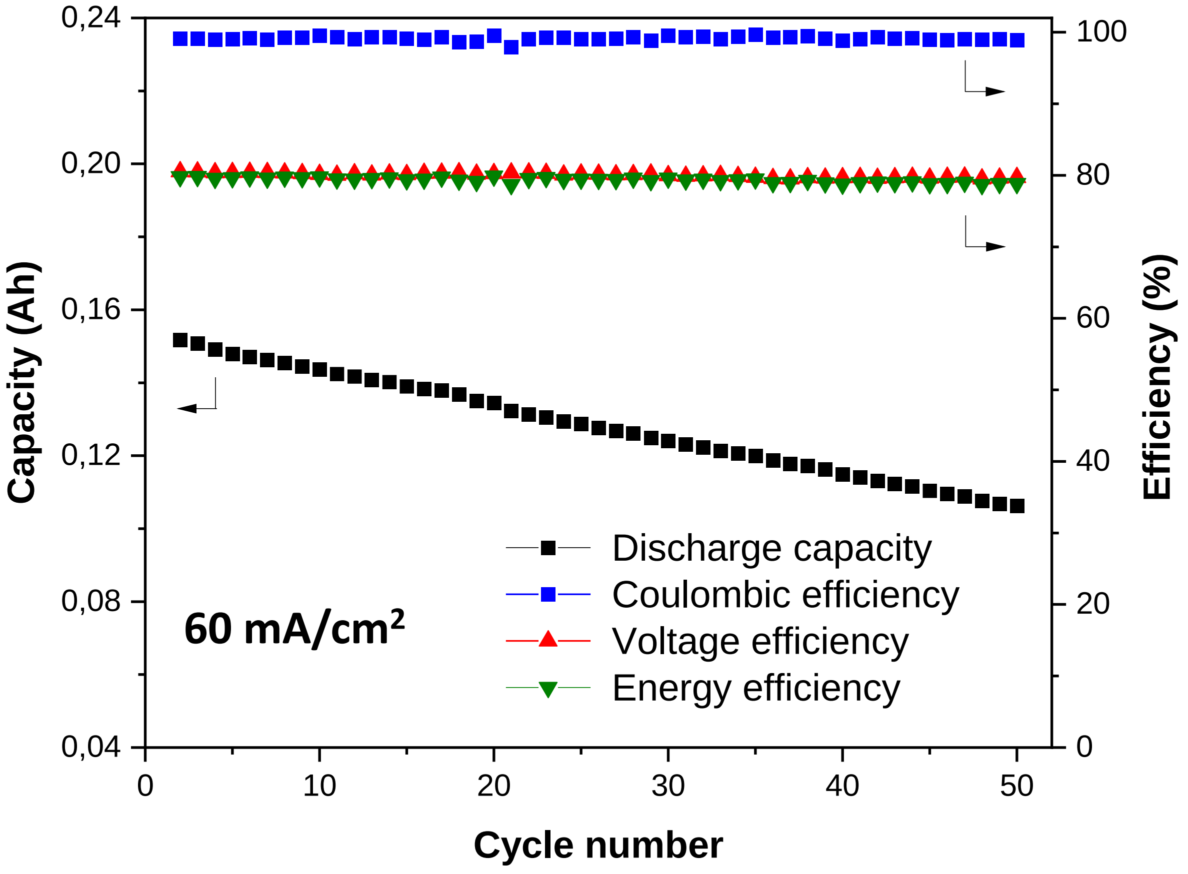


> Comparative study of membranes

Cycling tests at different currents



50-cycle experiment NR-212



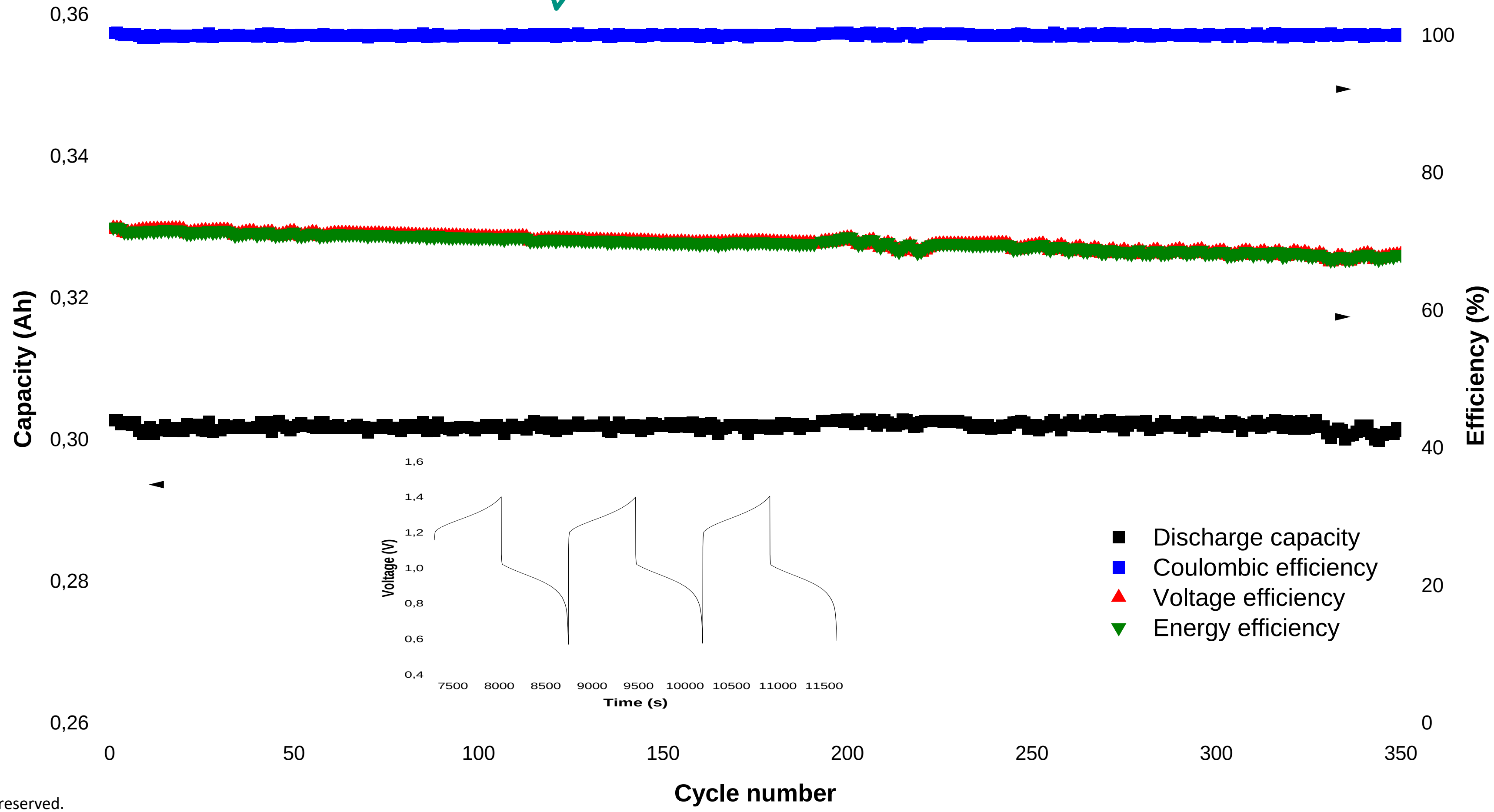
Long cycling test

Membrane: FS-950
350 cycles
60 mA/cm²

<0.001% per cycle

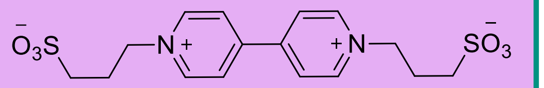
0,5M TEMPO-SO_4K in 3,6M NH_4Cl + 0,9M KCl

0,5M $(SPr)_2V$ in 2,6M NH_4Cl

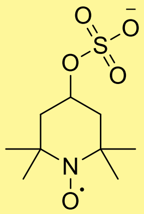


Conclusions

$(SPr)_2V$



TEMPO-SO_4K



- High solubility in aqueous media in order to achieve high energy densities (cell voltage 1,25 V)

Electrolyte

- Optimal electrolyte formulation to reach higher conductivities
- Critical role of chloride anions to avoid formation of aggregates

- Importance of the electrolyte-membrane combination when calculating parameters such as VE, capacity retention and cell resistance.
- Higher voltage efficiencies (**>70%**) and outstanding peak power densities **262 mW/cm2**
- Long cycling stability in terms of capacity and a low-capacity fade rate of 0.001% per cycle for over 350 cycles with nearly 100% Coulombic efficiency

> Acknowledgements

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GOBIERNO VASCO

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GRACIAS · THANK YOU · ESKERRIK ASKO

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& TECHNOLOGY ALLIANCE

Parque Tecnológico · c/Albert Einstein 48
01510 Vitoria-Gasteiz · (Álava) SPAIN
+34 945 29 71 08

CONTACT

Laura Pastor Muñoz
CIC energiGUNE's role
lpastor@cicenergigune.com

Making sustainability real

cicenergigune.com