2nd March 2022

HIGREEW project workshop, Pilsen (Czechia)

Overview of organic redox flow batteries

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Organic electrolytes for RFB

■ **Motivation**

✓ Cost reduction (< 100 $/kWh)

✓ Increase of energy density

✓ Environmentally friendliness

https://www.nevadavanadium.com/

■ **Required properties**

→ High solubility (in aqueous media)

→ Suitable redox potential (OCV)

→ Fast and multi-electron transfer

→ Stable, cheap and non-toxic

Commercial development

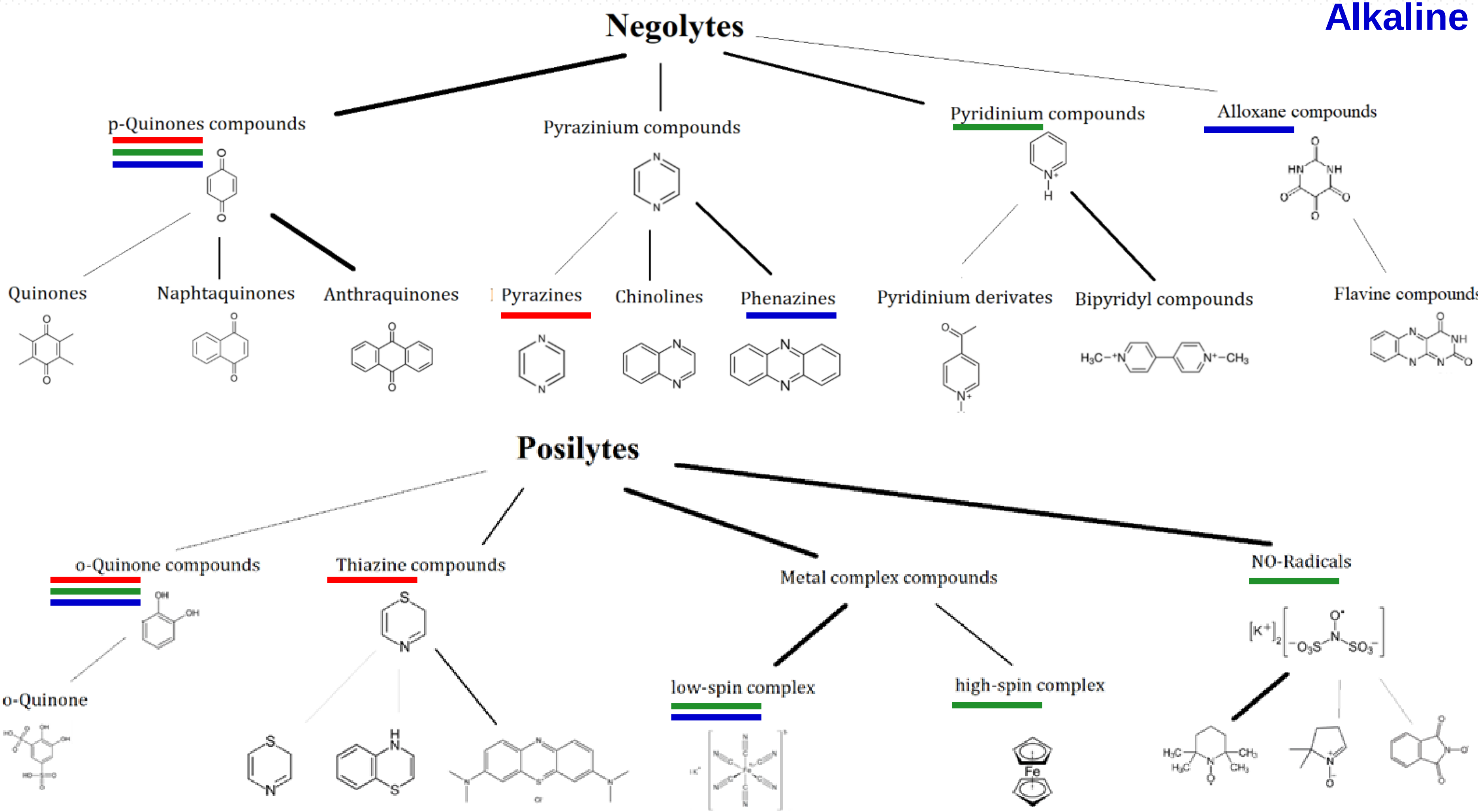
- Jena Batteries (GER)
- Kemiwatt (FRA)
- XL Batteries (USA)
- CM-Blu (GER)
- Green Energy Storage (ITA)

Fischer, P.; Mazúr, P.; Krakowiak, J.; Molecules 2022, 27, 560.

Organic electrolytes for RFB

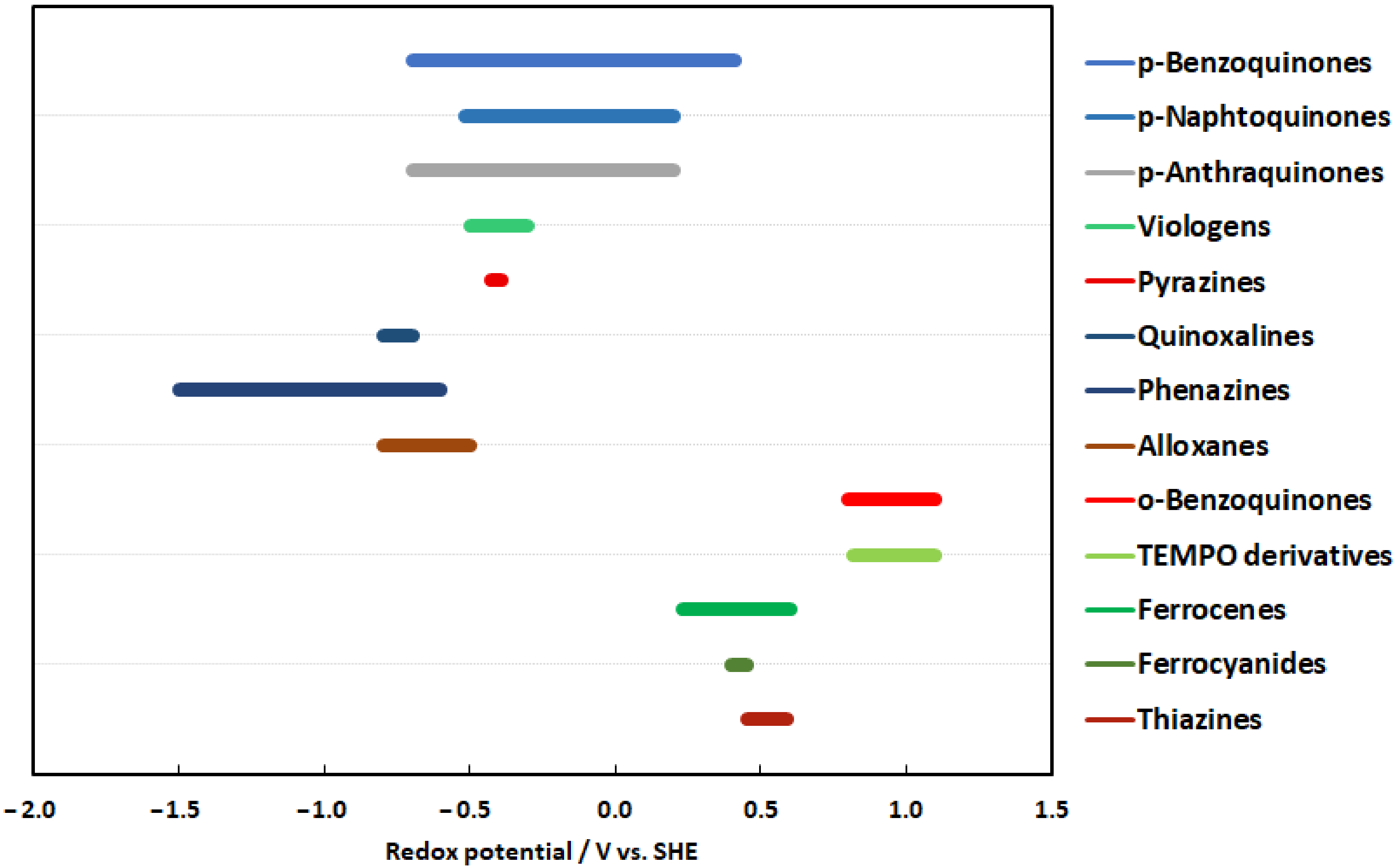
■ Perspective groups of compounds

Acidic
Neutral
Alkaline



Organic electrolytes for RFB

Perspective groups of compounds



Organic electrolytes for RFB

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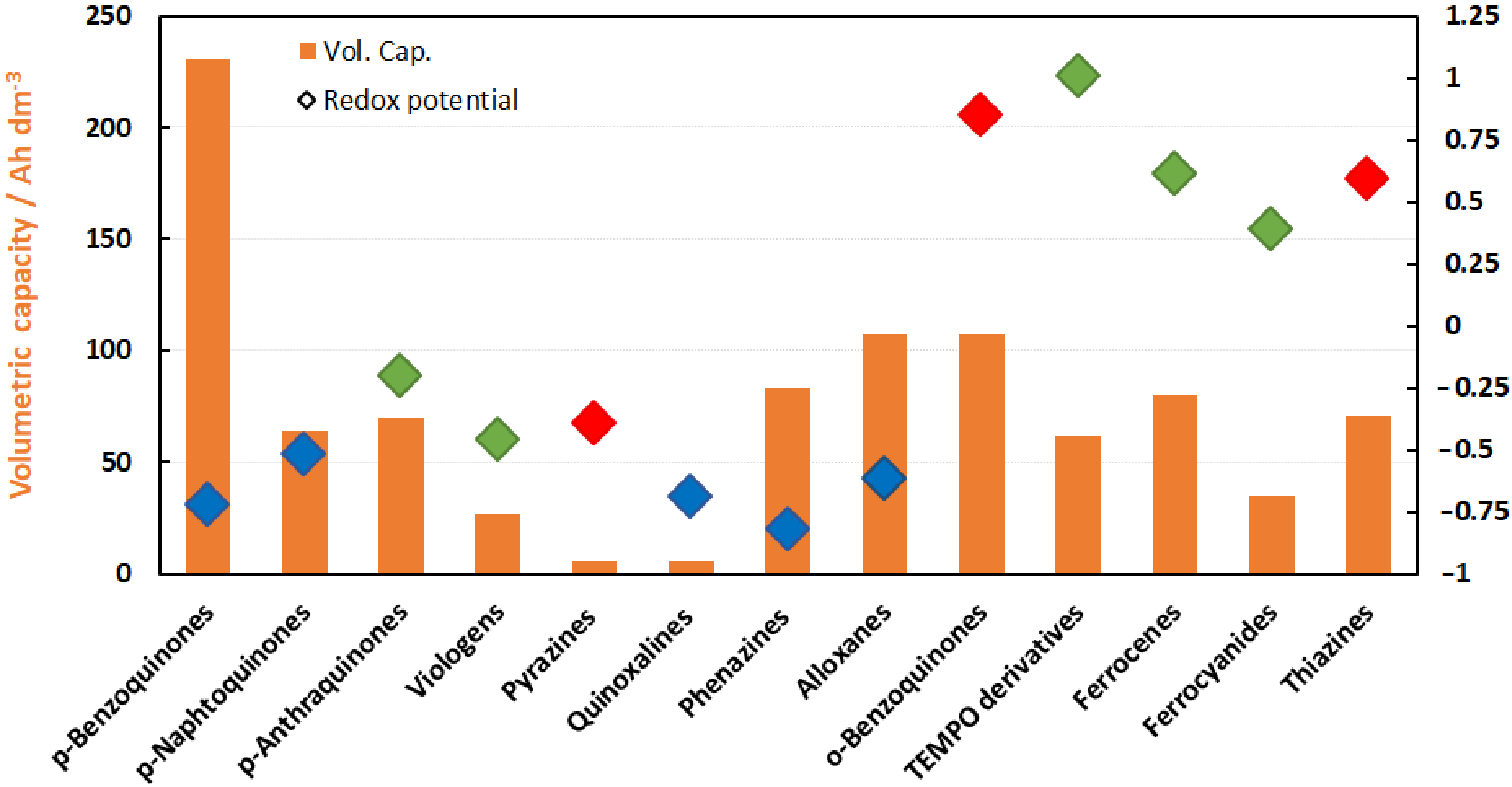


Organic electrolytes for RFB

■ Solubility

$$\frac{E}{V} = Fz\frac{c}{2}U_{OCV}$$

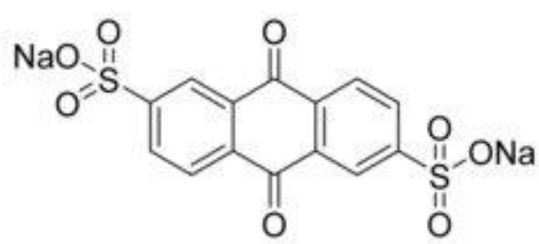
Can be influenced by:

✓ **Substituents and position**

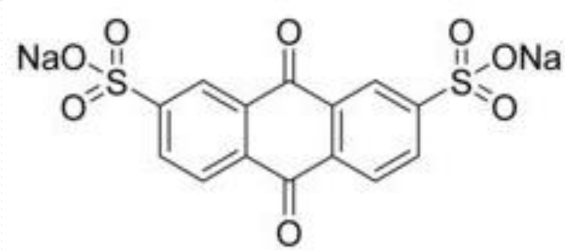
Neg. charged functional groups:
carboxyl- < phosphate- < phosphonic- < sulfate- < sulfonic < sulfonimido-

Pos. charged functional groups: pyridinium- < imidazolium- < tetraalkylammonium-

Non-charged functional groups:
cyano- < mercapto- < hydroxy- < morpholino- < polyether-groups



2,6-AQDS disodium salt
aqueous solubilty: 0.04 M



2,7-AQDS disodium salt
aqueous solubilty: 0.58 / 0.74 M

D. Konya et al., Molecules 2021, 26, 1203

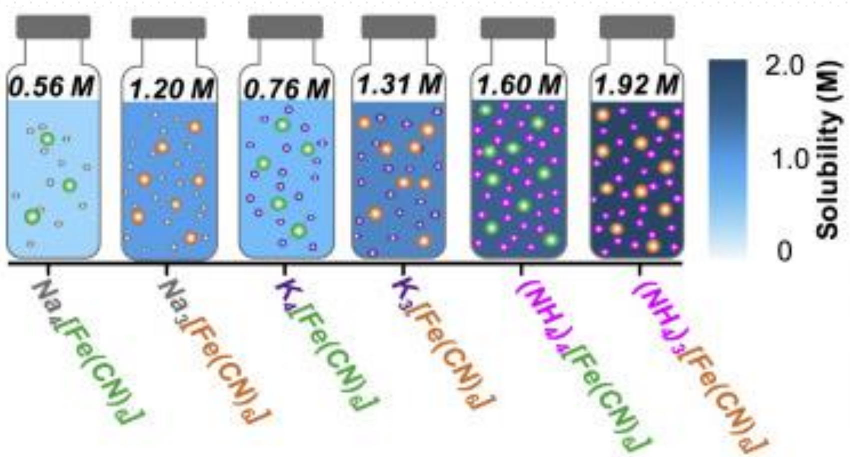
Organic electrolytes for RFB

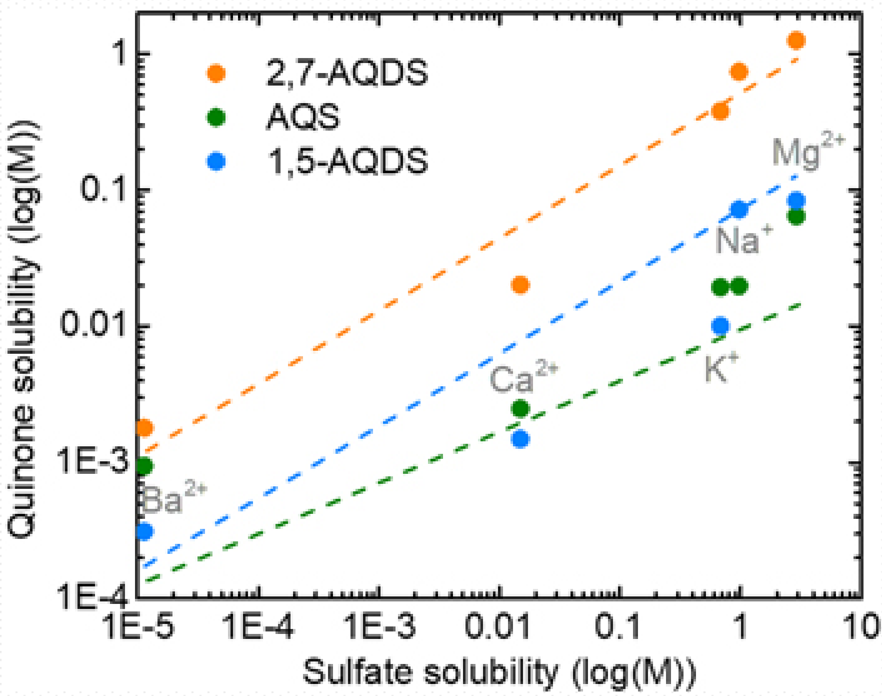
■ Solubility

Can be influenced by:

- ✓ **Counter ions**
- ✓ Supporting electrolyte / pH
- ✓ Solubilizing agent

$$\frac{E}{V} = Fz\frac{c}{2}U_{OCV}$$





J. Luo et al., Joule 3, 149–163, January 16, 2019

J. Mao et al., Journal of The Electrochemical Society, 2020 167 070522

Organic electrolytes for RFB

Redox potentials

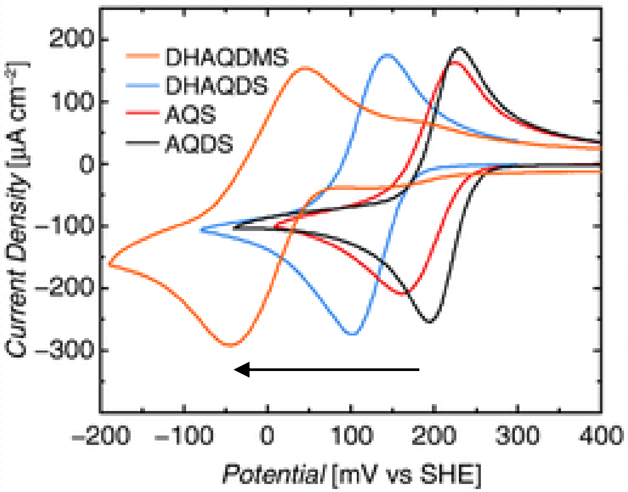
Can be tailored by:

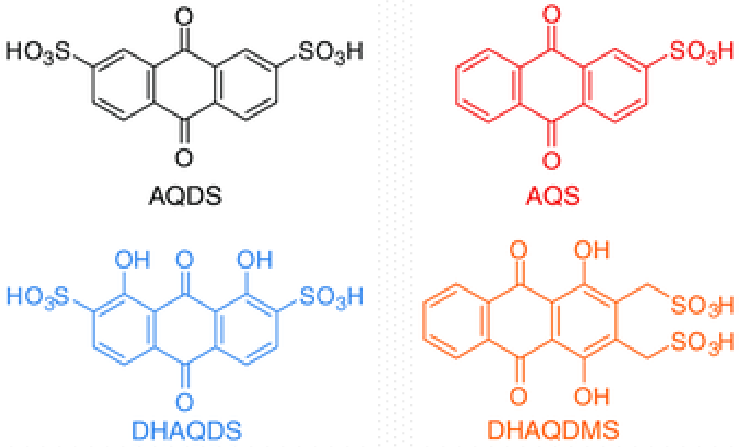
✓ substituents and position

$$E = E^0 + \frac{RT}{ZF} ln \frac{\prod (a_{ox,i})^{n_i}}{\prod (a_{red,i})^{m_i}}$$

Electron-withdrawing substituents move E° towards more positive values:
nitrato > cyanido > perfluormethyl > carboxy > chloride > fluoride

Electron-donating substituents move E° towards more negative values:
ethyl < methyl < thiol < hydroxy < ammino < triethylamino



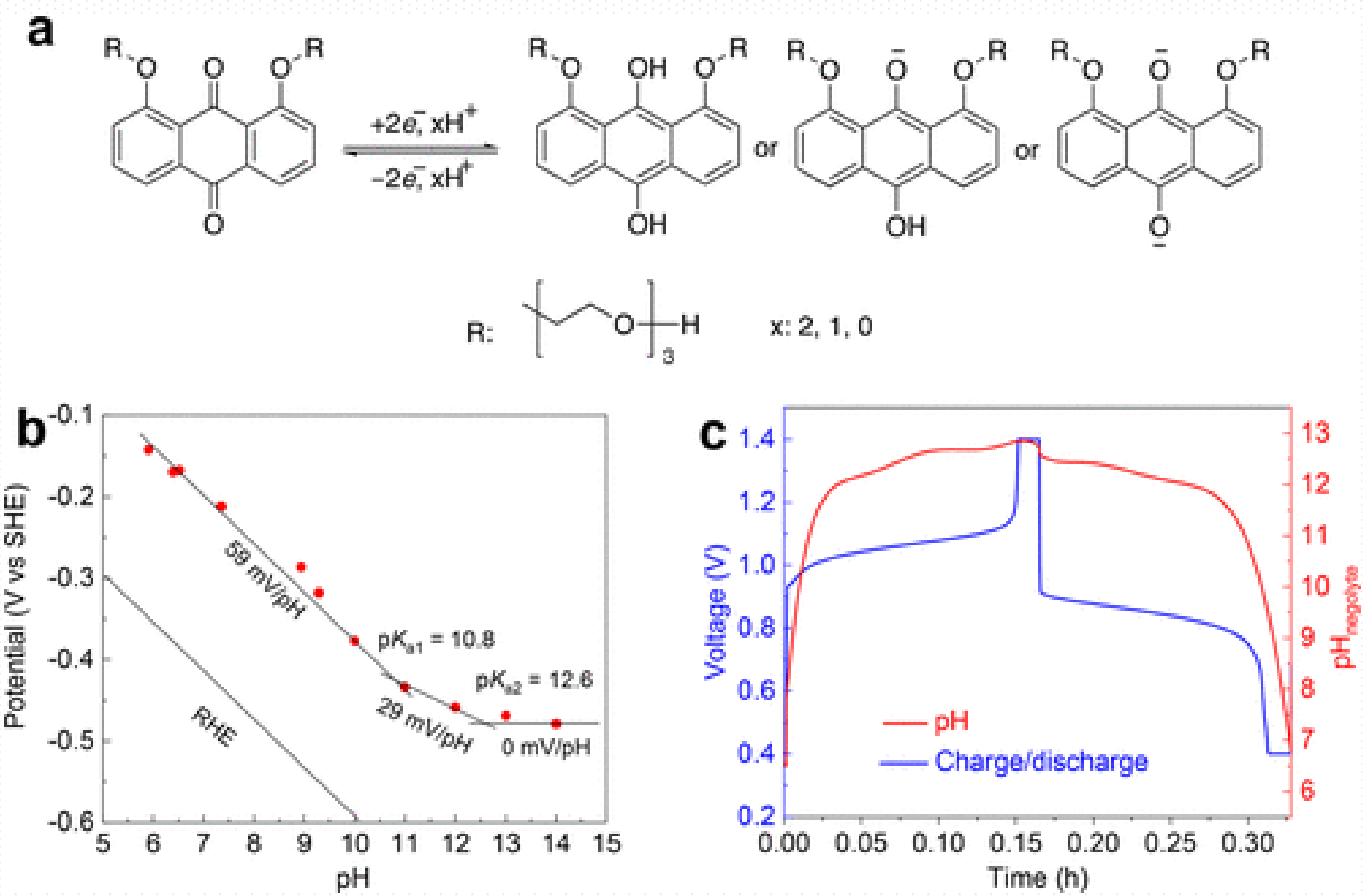


M. R. Gerhardt, Adv. Energy Mater. 2017, 7, 1601488

Organic electrolytes for RFB

■ Electrode reaction mechanisms and kinetics

✓ pH dependent E° if involves H+/OH- ions

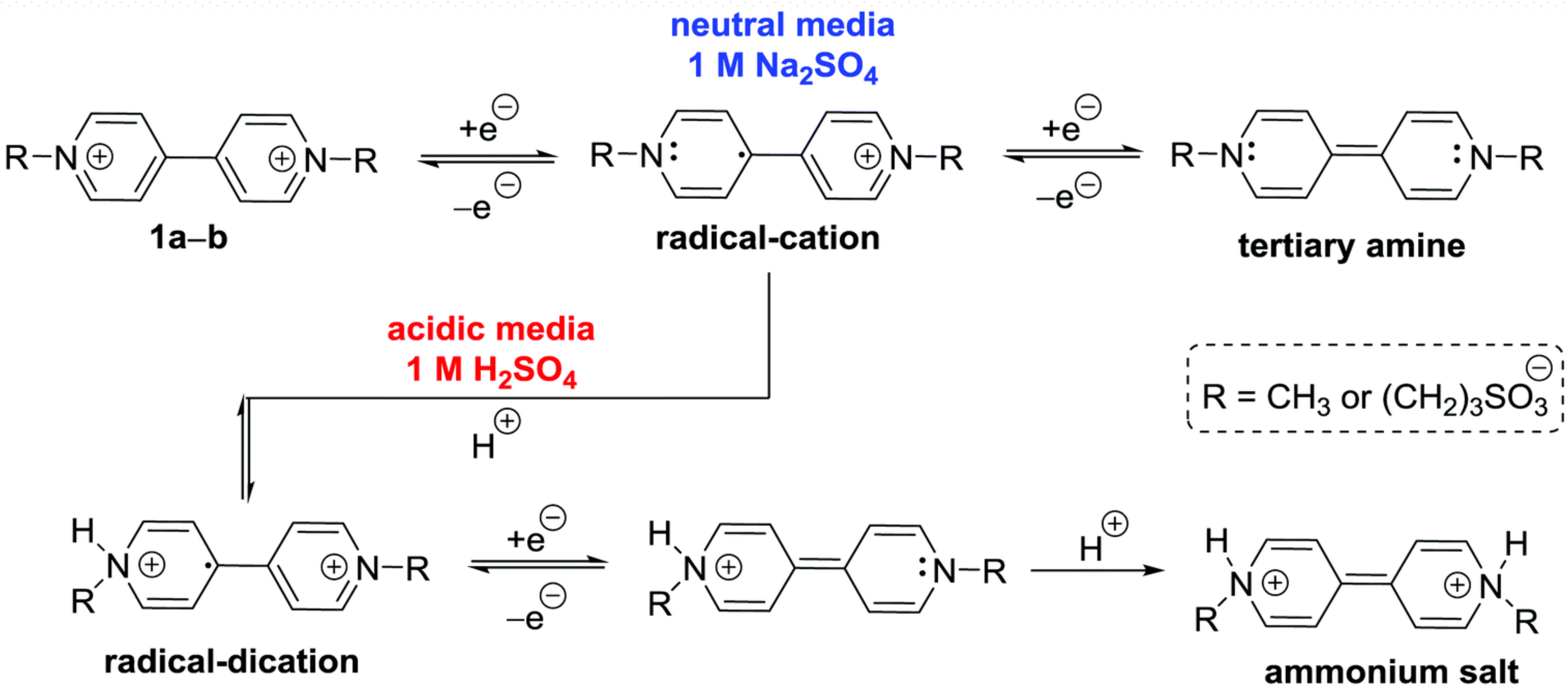


S. Jin, ACS Energy Lett. 2019, 4, 6, 1342-1348

Organic electrolytes for RFB

Electrode reaction mechanisms and kinetics

✓ Reversibility can be lost due to subsequent chemical reaction (e.g. protonation)

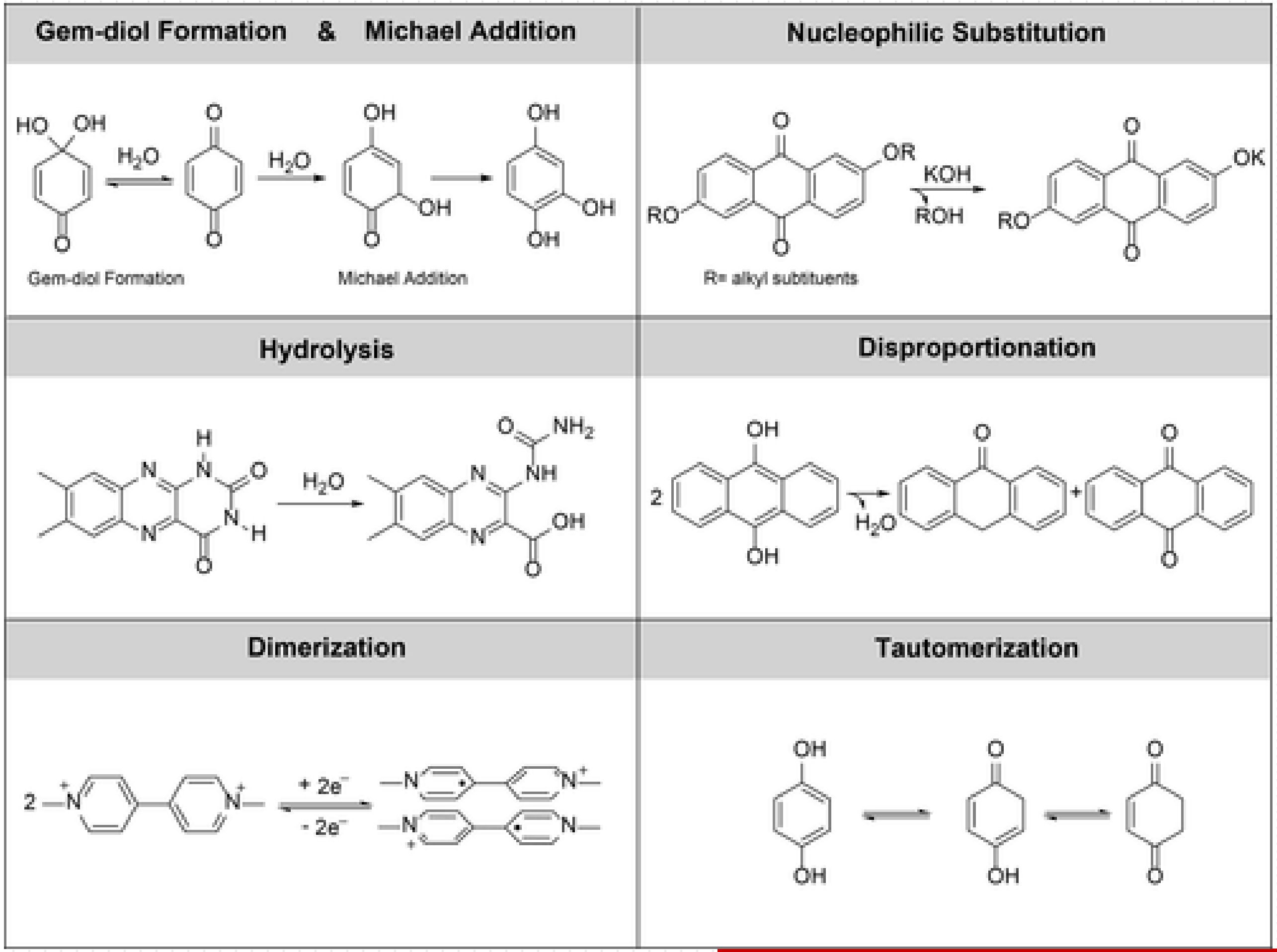


K. Rak, Org. Biomol. Chem., 2021, 19, 8830-8839

Organic electrolytes for RFB

Active species degradation

✓ Depends on pH, temperature, SoC and concentration



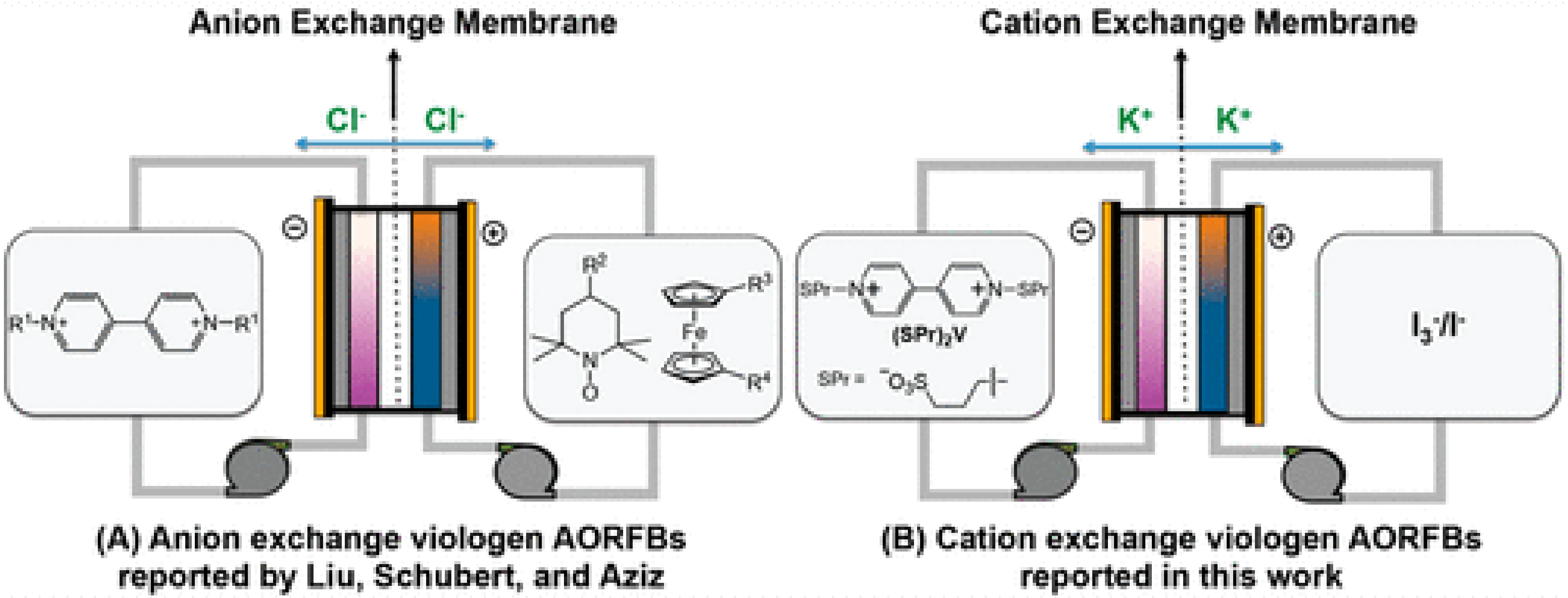
D. G. Kwabi, Chem. Rev. 2020, 120, 6467−6489

Organic electrolytes for RFB

Membrane cross-over

- ✓ Active species diffusion/migration
- ✓ Net overflow due to osmosis/electroosmosis

Mitigation strategies: equalized ionic strength, selective membrane, mixed electrolyte



C. DeBruler, ACS Energy Lett. 2018, 3, 663−668

Organic electrolytes for RFB

Other aspects in RFB development

✓ **Electrolyte formulation**

- Supporting electrolyte
- Ionic conductivity vs. solubility vs. viscosity

✓ **Component selection/optimization**

- Carbon felt/paper activation
- Electrode performance stability (deactivation)

✓ **Stack design**

- Pressure drop (pumping losses) vs. Shunt currents

EVROPSKÁ UNIE
Evropské strukturální a investiční fondy
Operační program Výzkum, vývoj a vzdělávání

MINISTERSTVO ŠKOLSTVÍ, MLÁDEŽE A TĚLOVÝCHOVY

The work was supported from European Regional development Fund-Project "Organic redox couple based batteries for energetics of traditional and renewable resources (ORGBAT)" No.CZ.02.1.01/0.0/0.0/16_025/0007445.

Thank you for attention.

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