Aqueous Organic Redox Flow Battery (AORFB)

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Supervisor: Prof. Zhang Junliang

2020.12.11

1. Background and Brief Introduction
2. Types of AORFBs
    I. Acidic AORFBs
    II. Alkaline AORFBs
    III. pH Neutral AORFBs
3. Summary and Outlook

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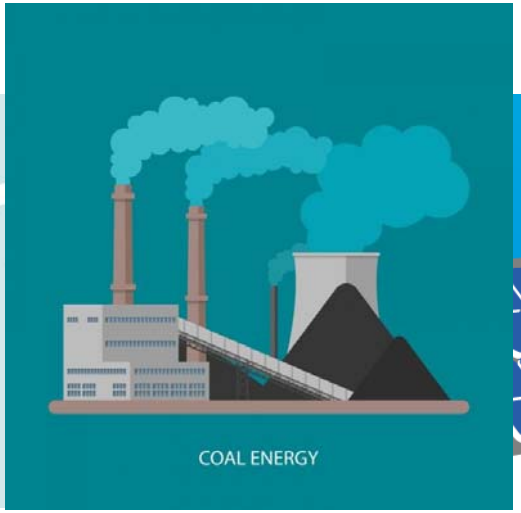
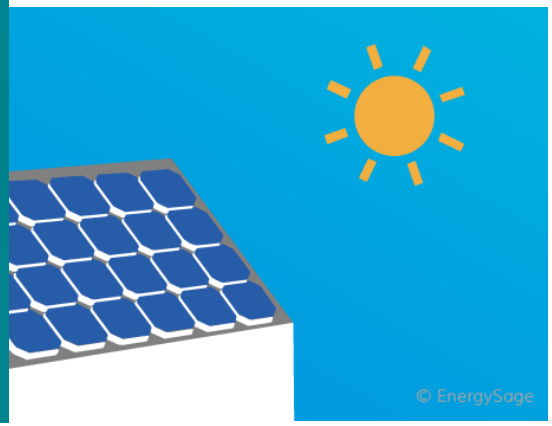
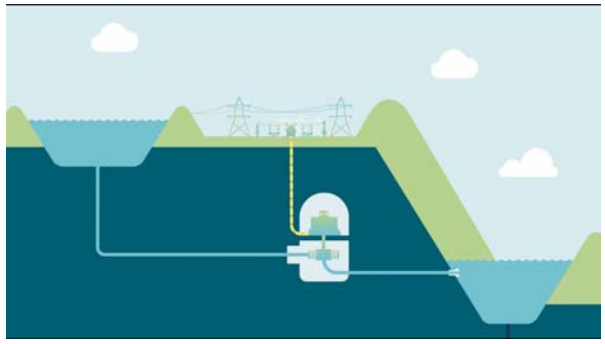
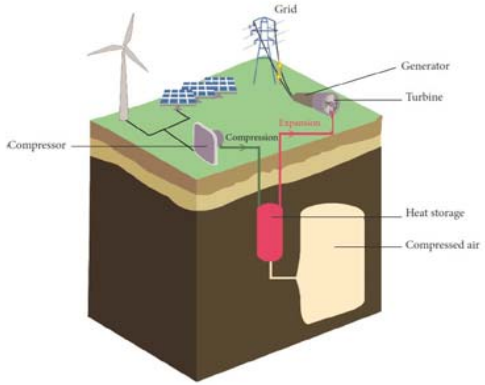
Background



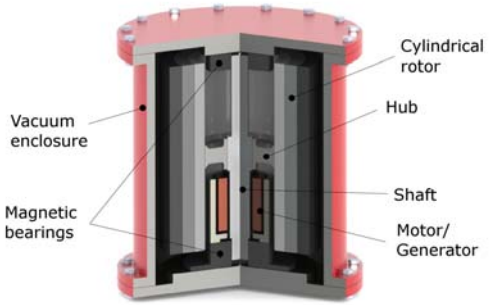




pumped hydroelectricity storage

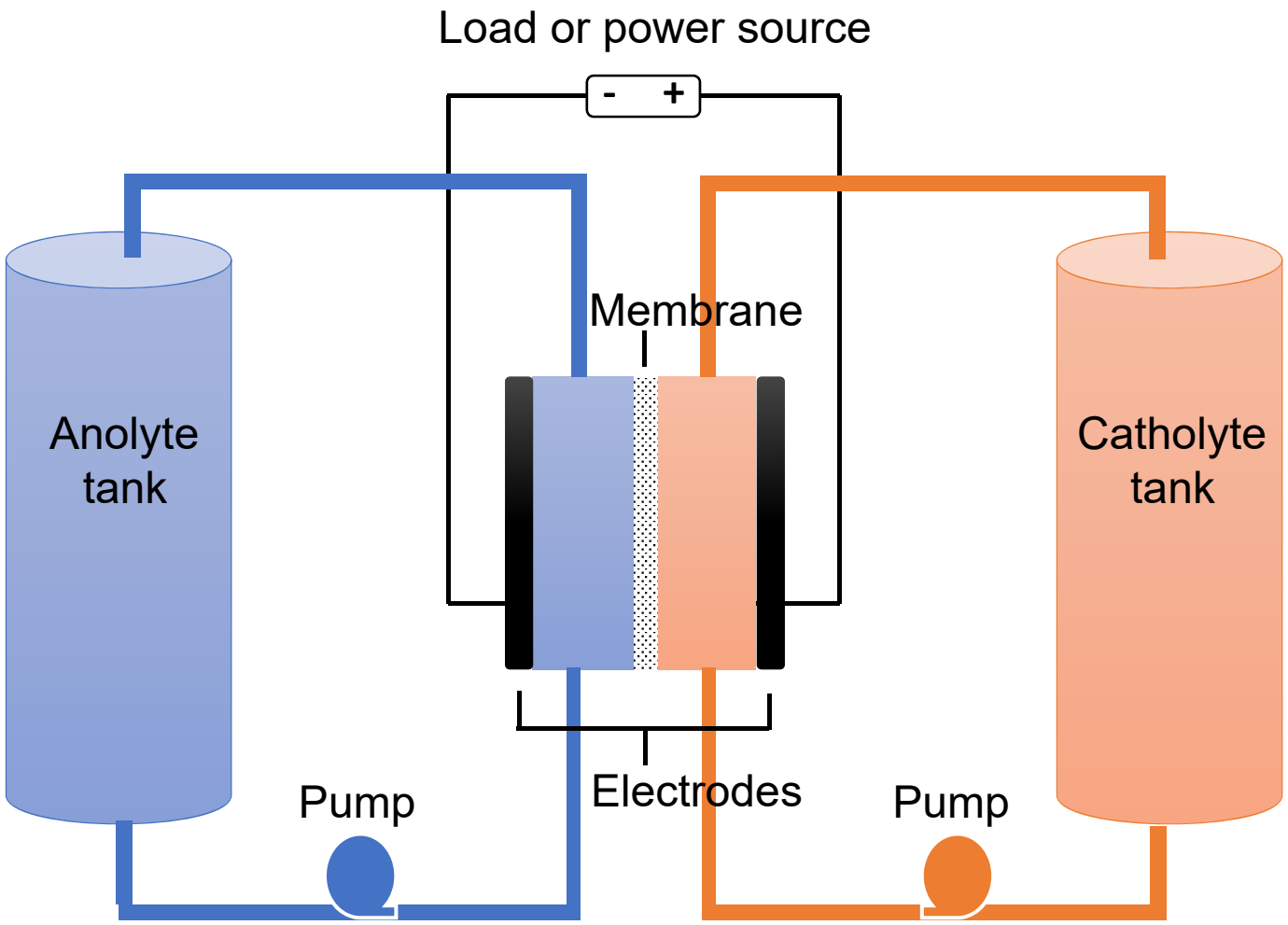


compressed air energy storage

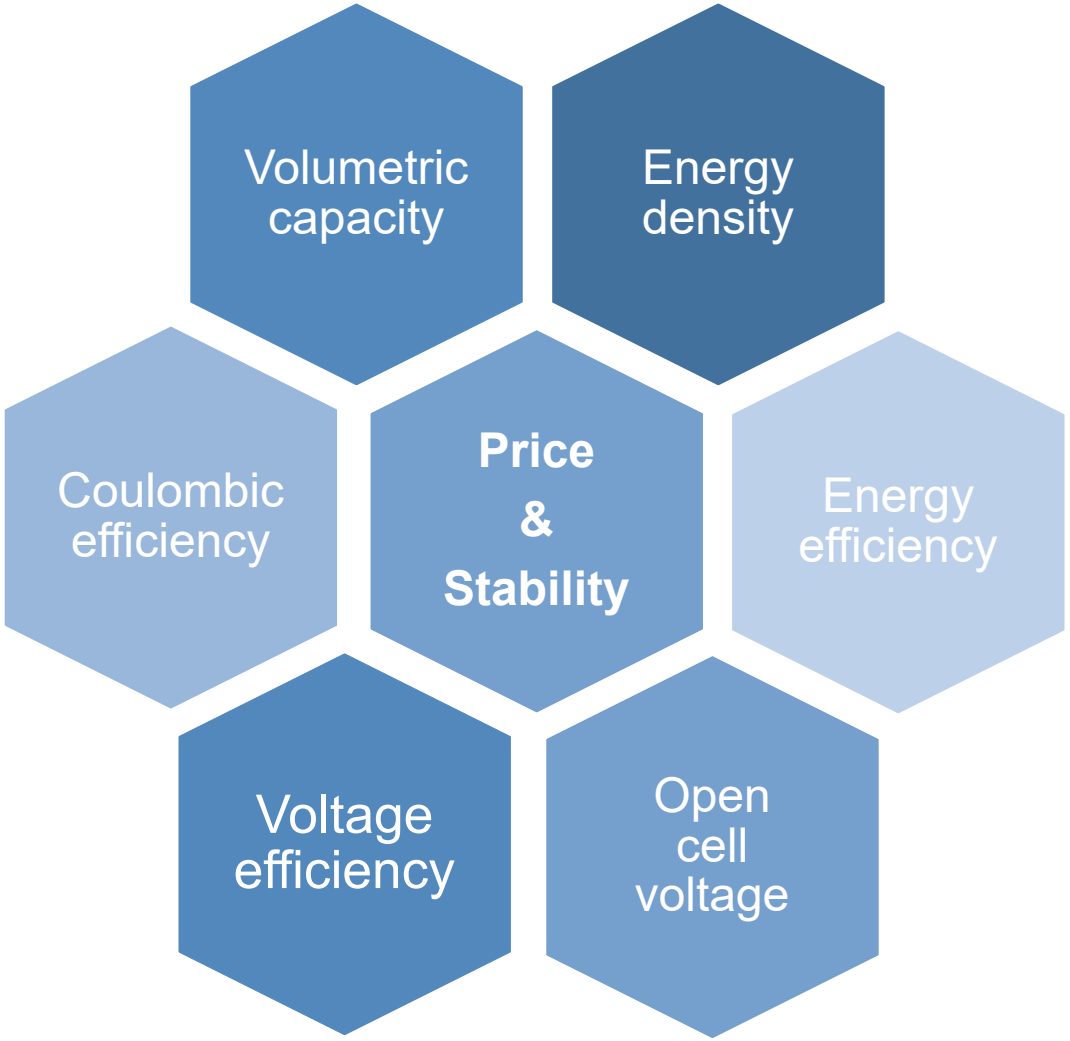


flywheel energy storage

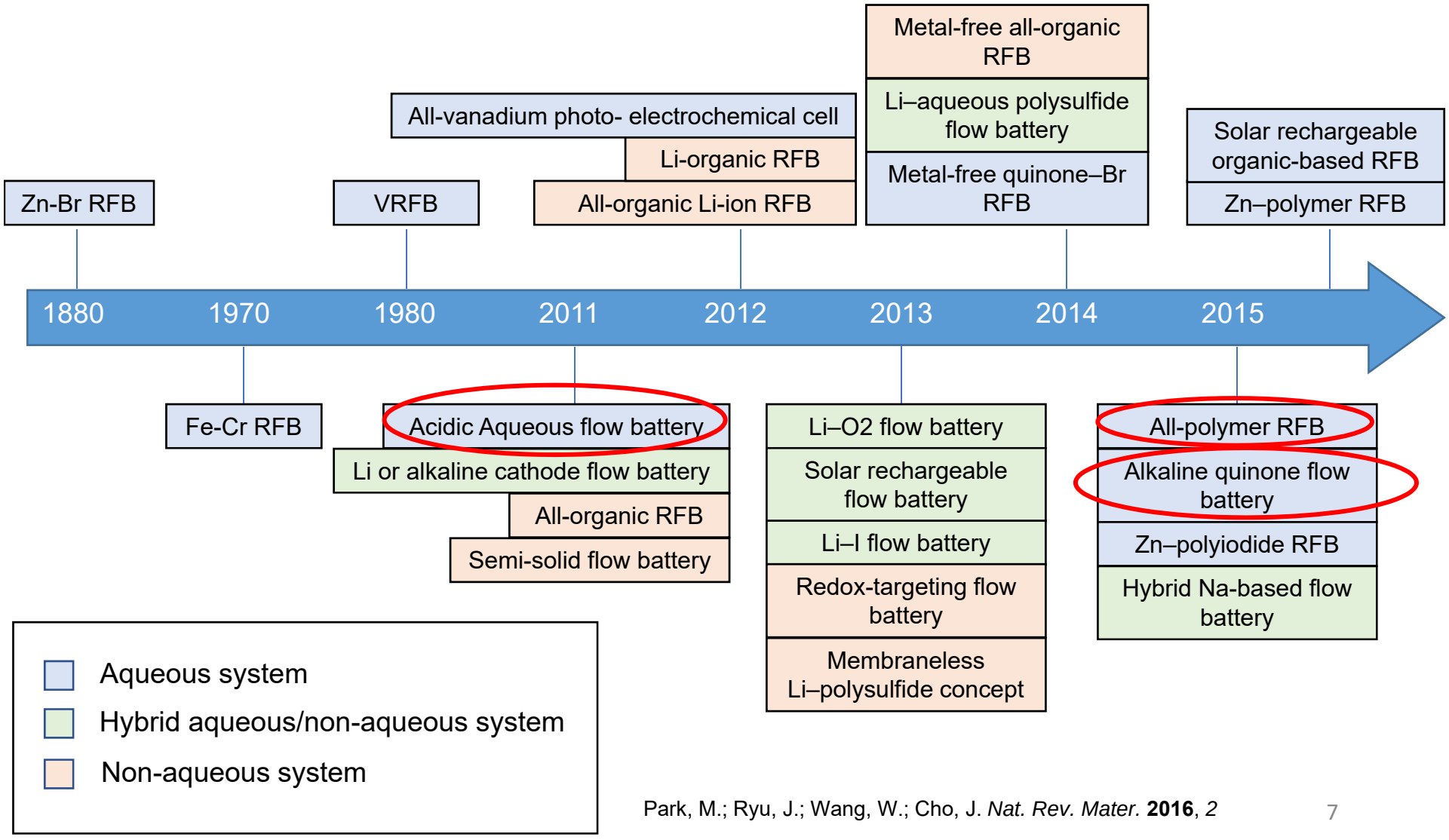
Introduction of RFB



Some General Benchmark



Types of RFBs



Park, M.; Ryu, J.; Wang, W.; Cho, J. *Nat. Rev. Mater.* **2016**, *2*

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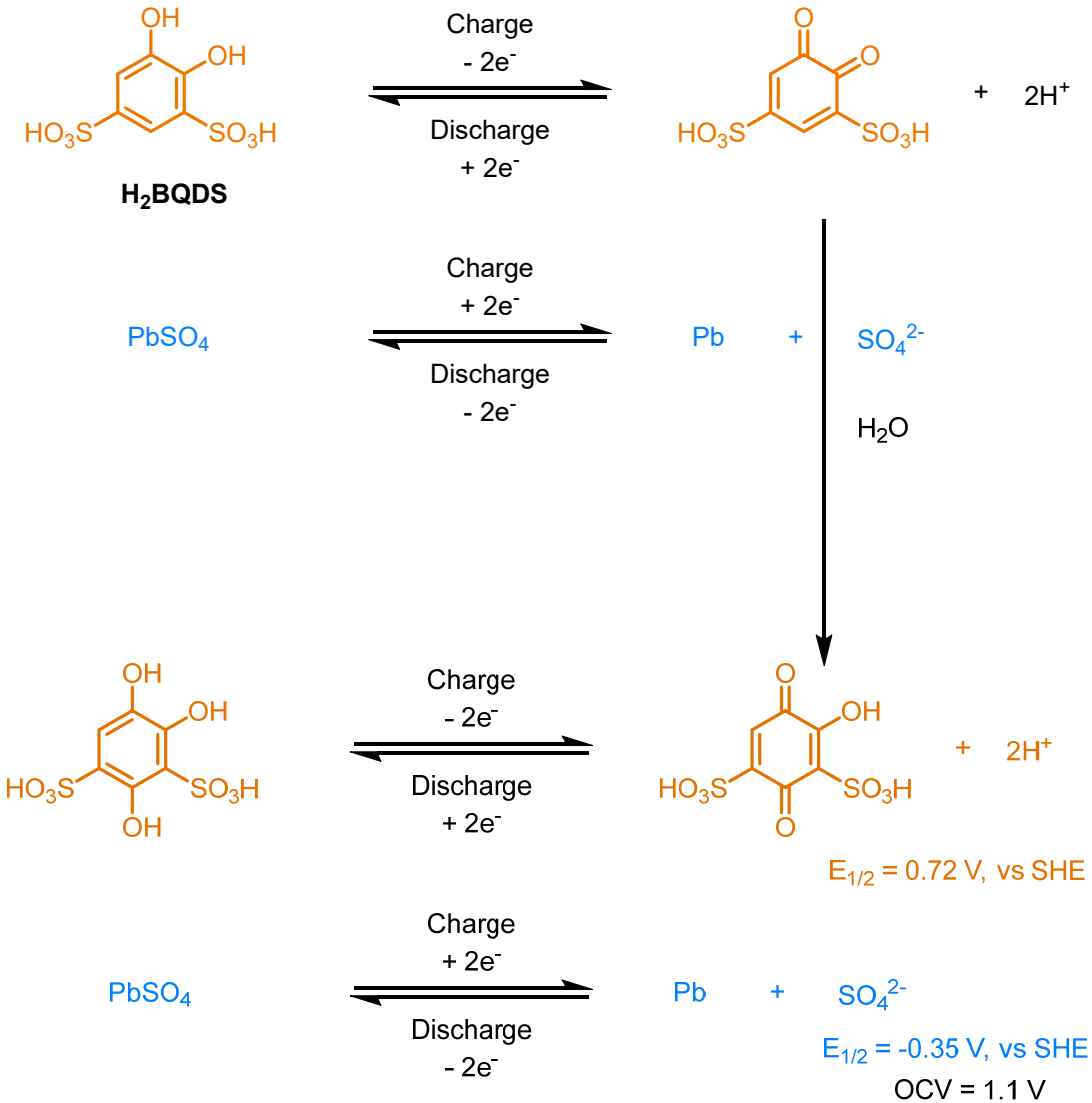
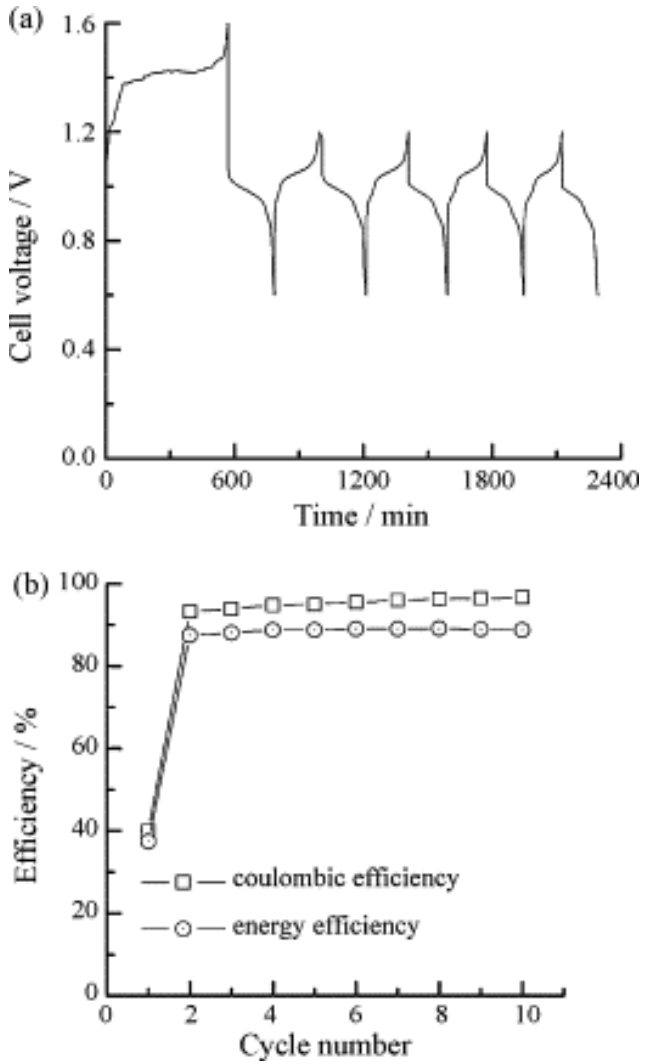
Acidic AORFBs: pH < 4

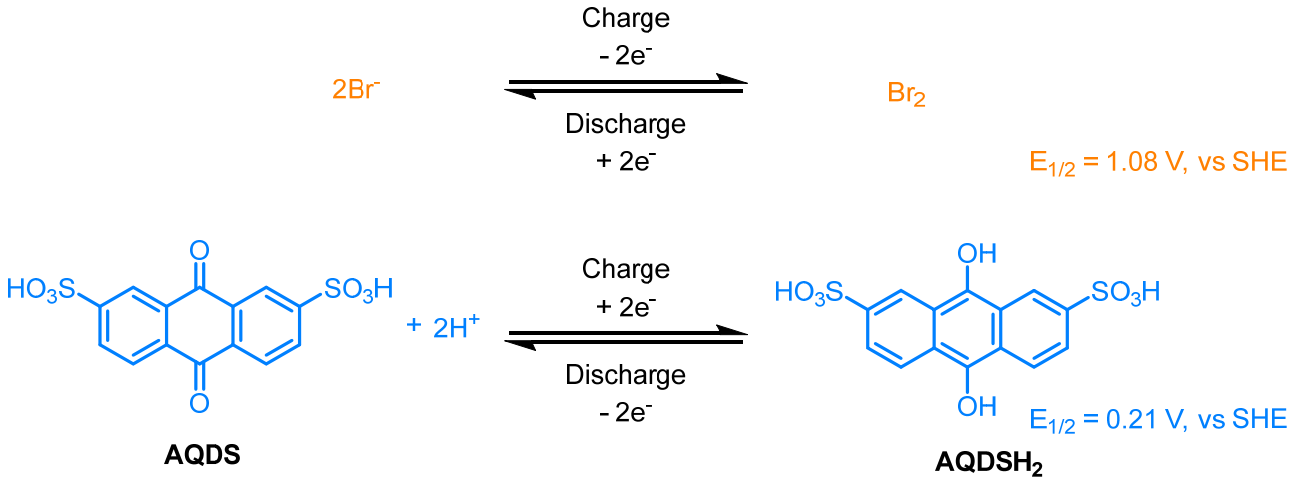




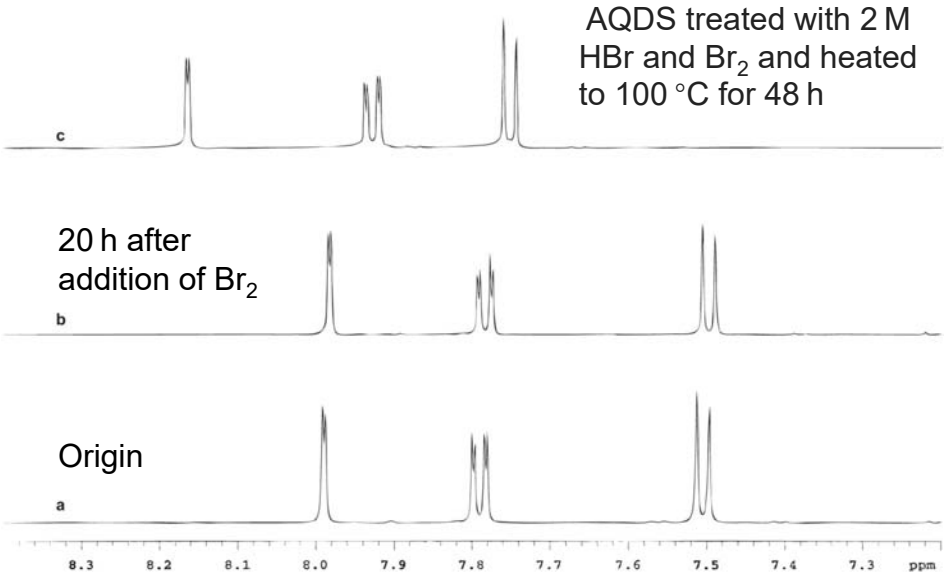
10 mA/cm^2
(+): 0.25 M H_2BQDS in 3 M H2SO4
(-): lead electrode
Nafion 115

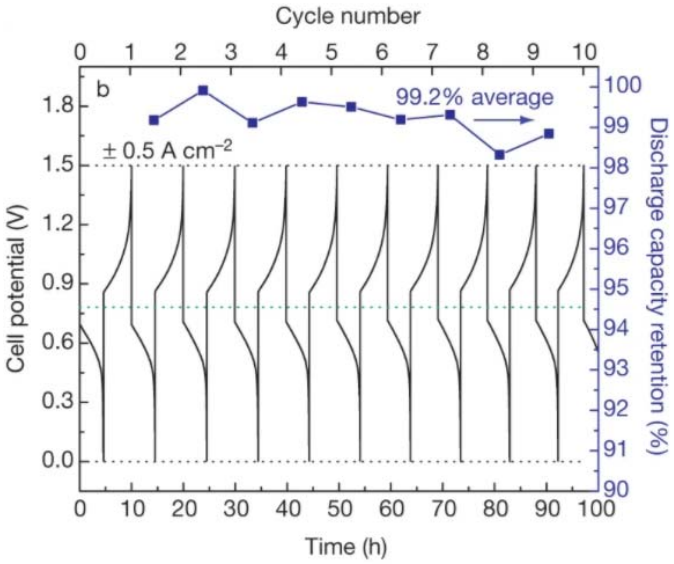
Wen, Y. H et al. *Electrochim. Acta* **2010**, *55*, 715

Acidic AORFBs: pH = 0



OCV = 0.858 V
$ 6.5 / kg

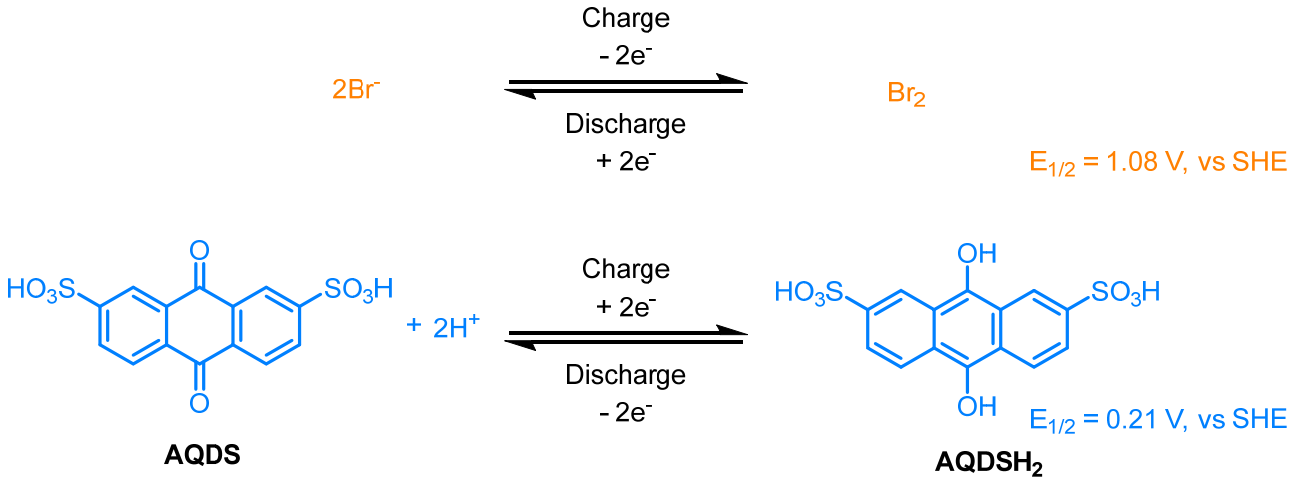




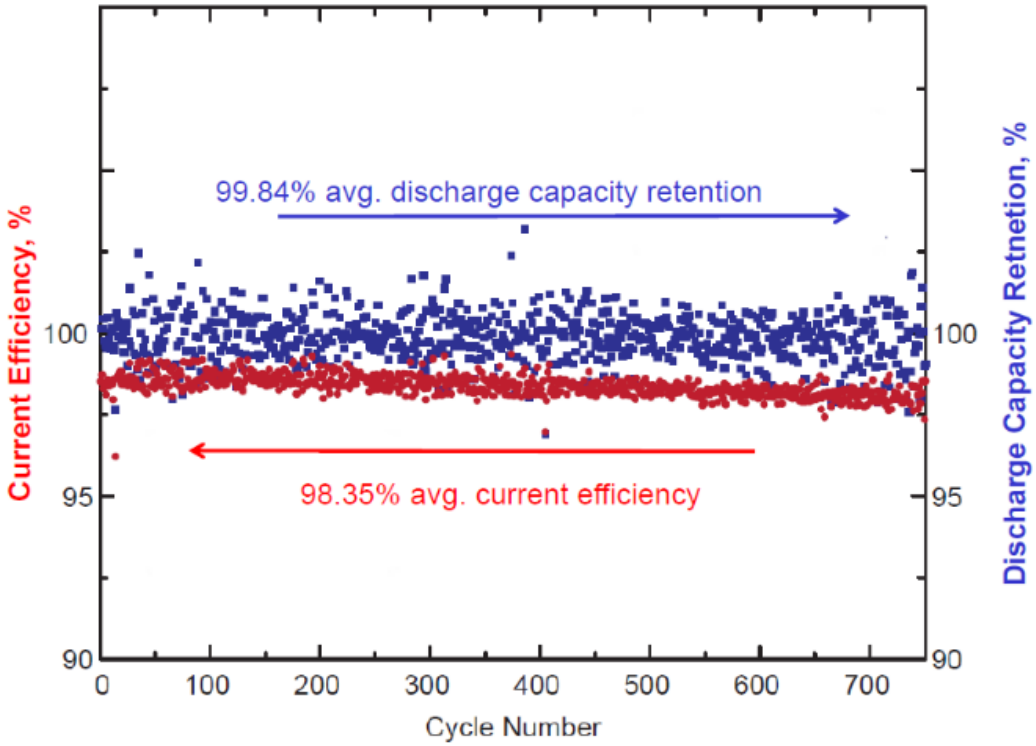
0.5 A/cm^2; 40 °C
(+): 3 M HBr + 0.5 M Br_2 solution
(-): 1 M AQDS + 1 M H_2SO_4 solution
Nafion 212 (50 μm)

Gordon, R. G.; Aziz, M. J et al. *Nature* **2014**, *505*, 195

Acidic AORFBs: pH = 0



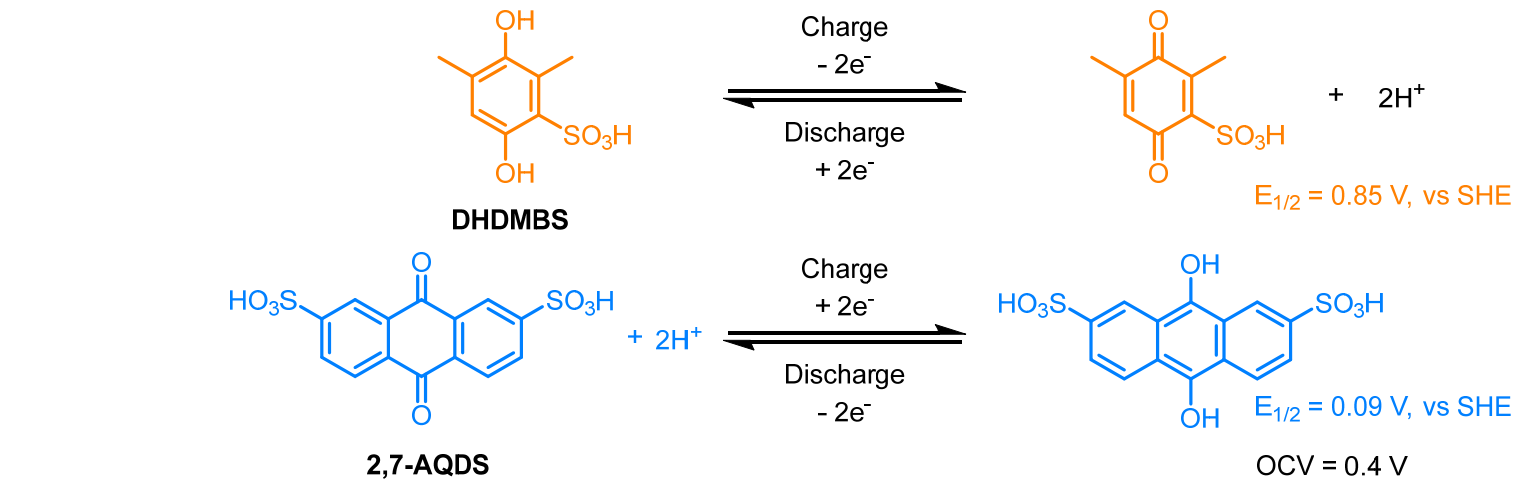
OCV = 0.858 V
$ 6.5 / kg

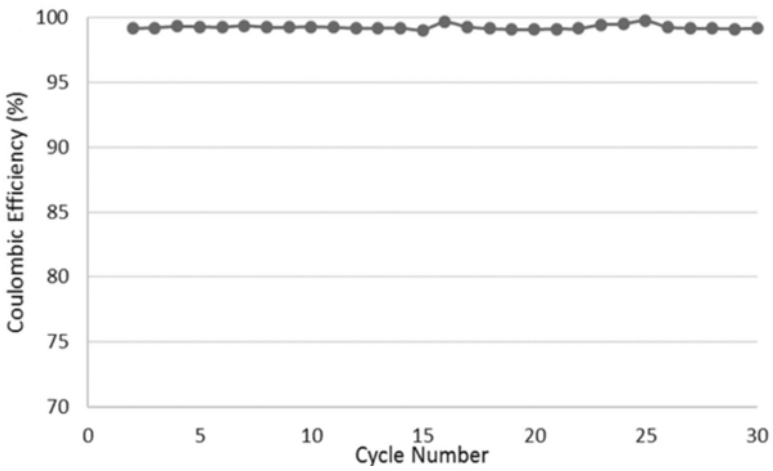


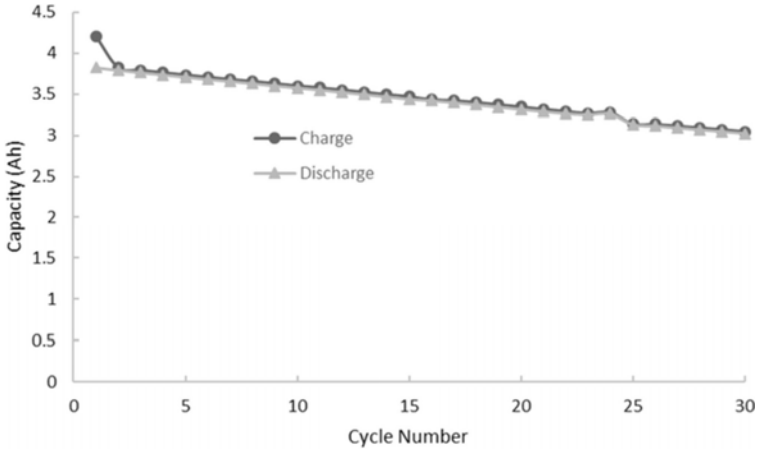
0.75 A/cm^2; 40 °C
(+): 3 M HBr + 0.5 M Br_2 solution
(-): 1 M AQDS + 1 M H_2SO_4
Nafion 115 (125 μm)

Aziz, M. J et al. *ECS Trans.* **2014**, *61*, 27

Acidic AORFBs: pH = 0



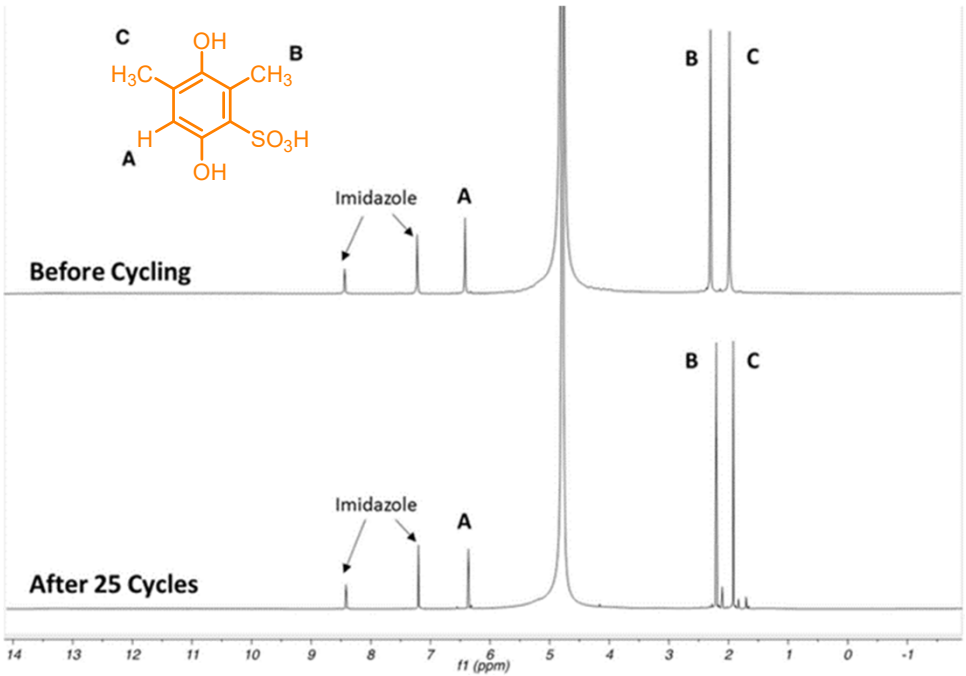


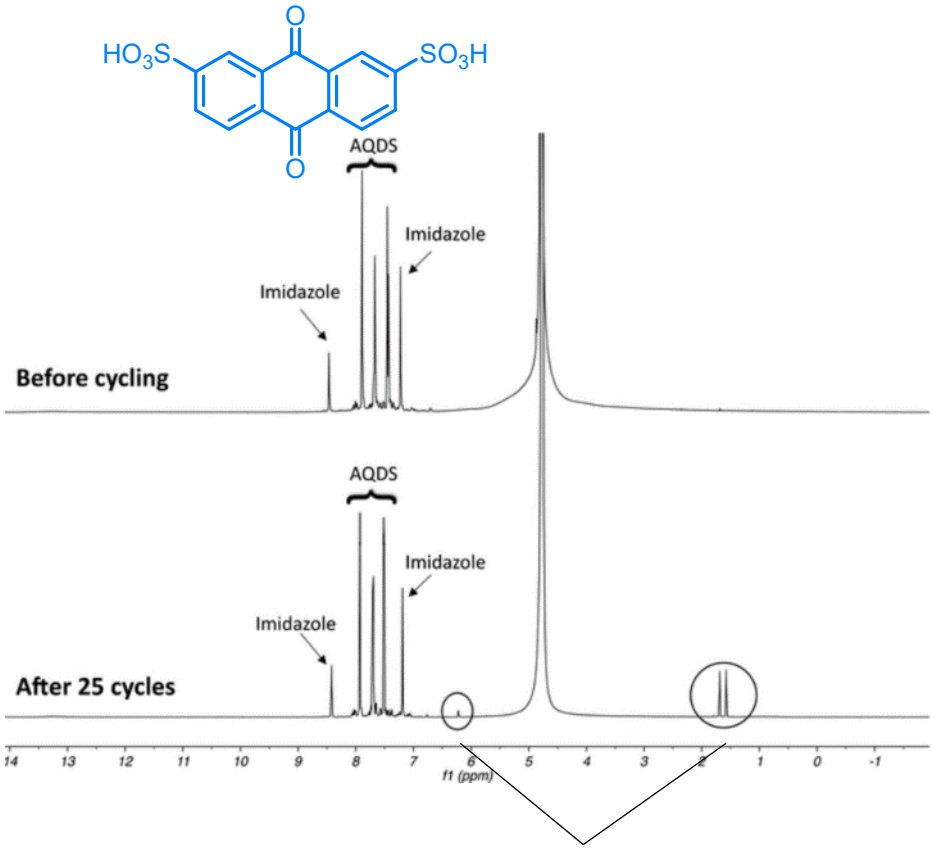


100 mA/cm^2 ;(+): 1 M DHDMBS, 1 M sulfuric acid; (-): 1 M 2,7-AQDS, 1 M sulfuric acid; Nafion

Narayanan, S. R et al. *J. Electrochem. Soc.* **2017**, *164*, A600

Acidic AORFBs: pH = 0

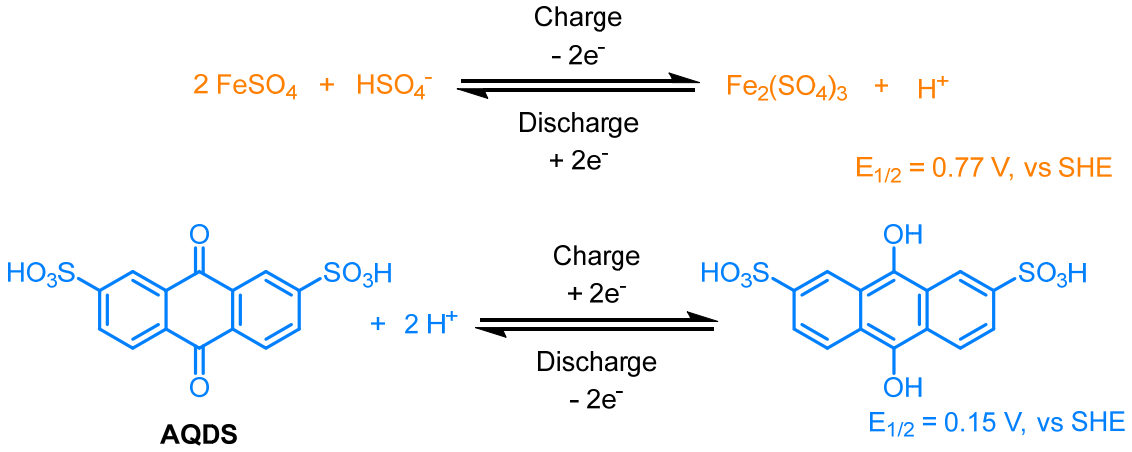




DHDMBS from crossover

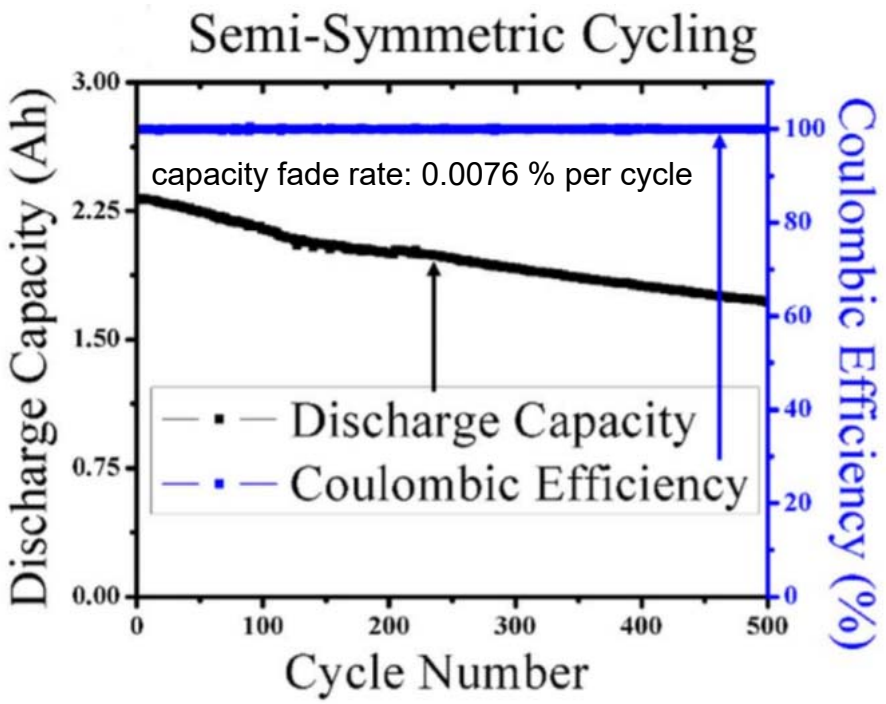
Narayanan, S. R et al. *J. Electrochem. Soc.* **2017**, *164*, A600

Acidic AORFBs: pH < 0



AQDS

OCV = 0.62 V



100 mA/cm^2
(+): 1 M iron(II) sulfate, 2 M sulfuric acid
(-): 1 M iron(II) sulfate, 2 M sulfuric acid, 0.5 M AQDS
Nafion 212

Narayanan, S. R. et al. *J. Electrochem. Soc.* **2020**, *167*, 060520

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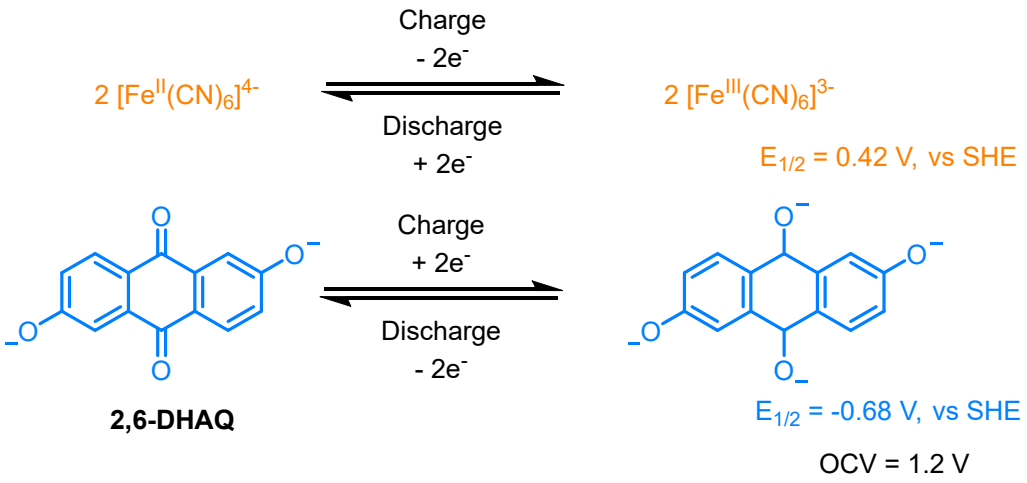
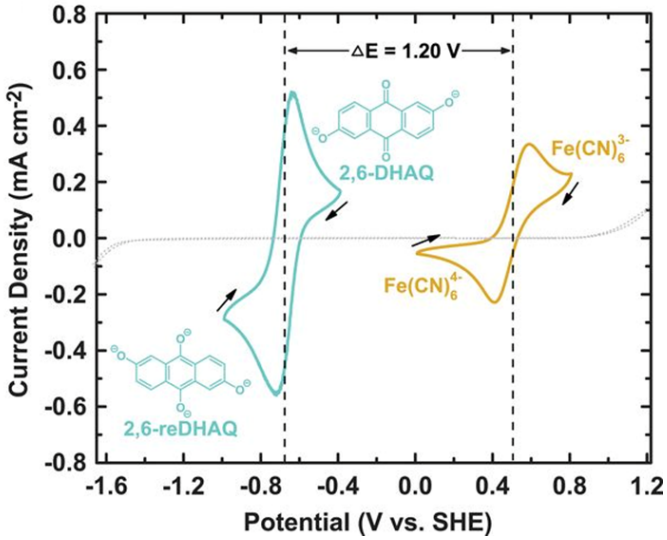
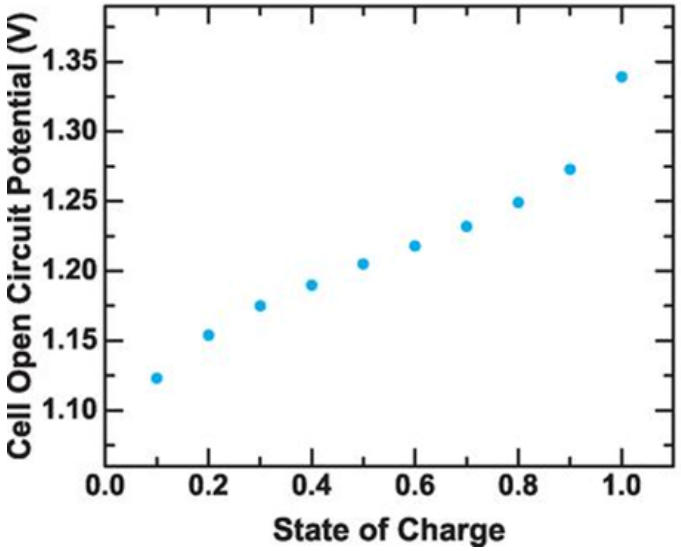
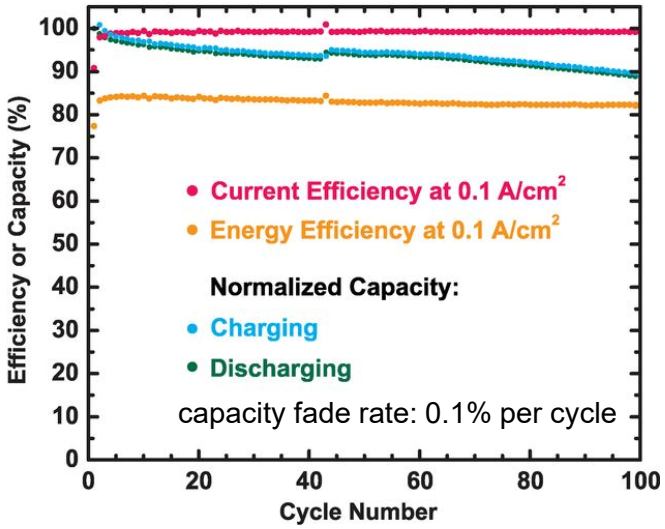
Alkaline AORFBs : pH = 14





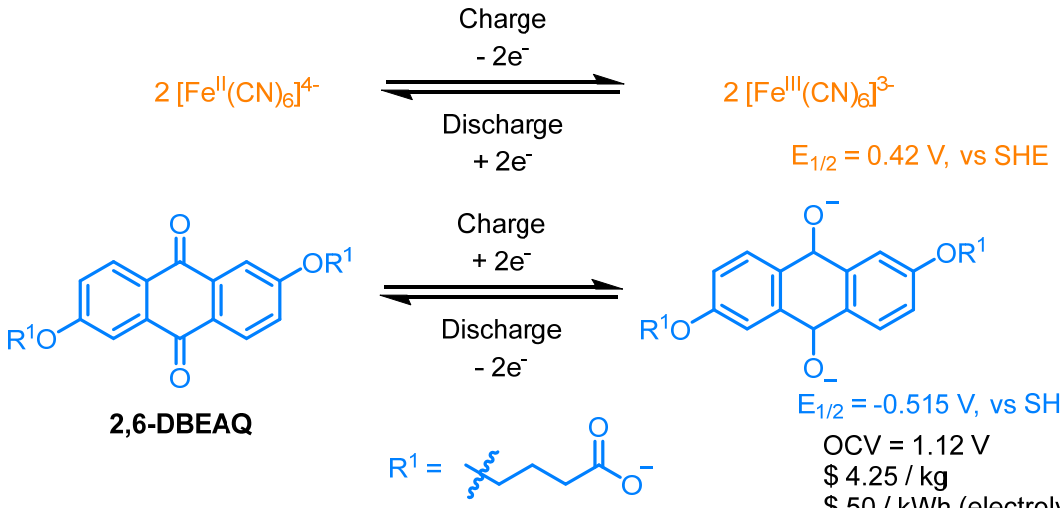




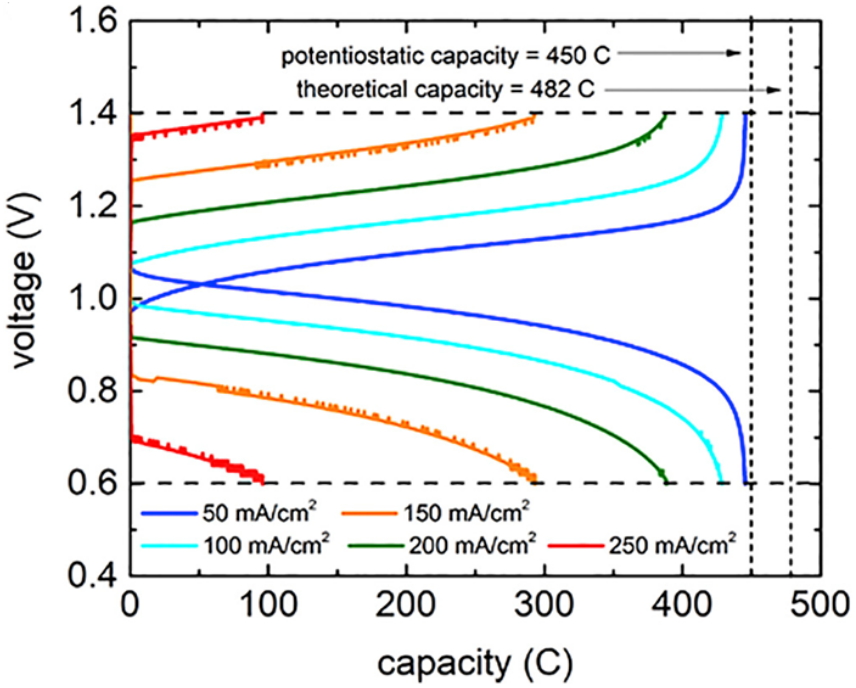
100 mA/cm^2
(+): 0.4 M ferrocyanide, 1 M KOH
(-): 0.5 M 2,6-DHAQ, 1 M KOH
Nafion

Gordon, R. G.; Aziz, M. J.; Marshak, M. P et al. *Science.* **2015**, *349*, 1529

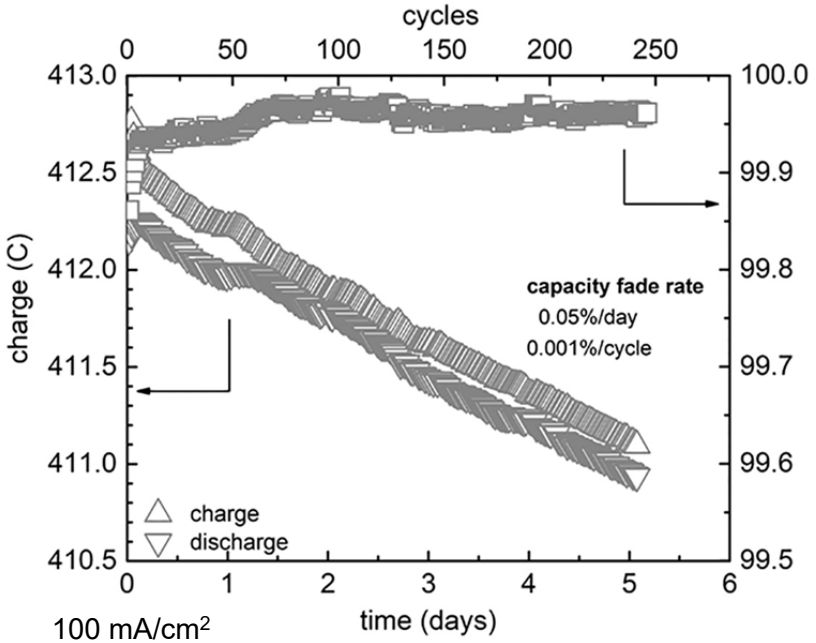
Alkaline AORFBs : pH = 12



OCV = 1.12 V
$ 4.25 / kg
$ 50 / kWh (electrolyte)



Aziz, M. J et al. *Joule* **2018**, *2*, 1894



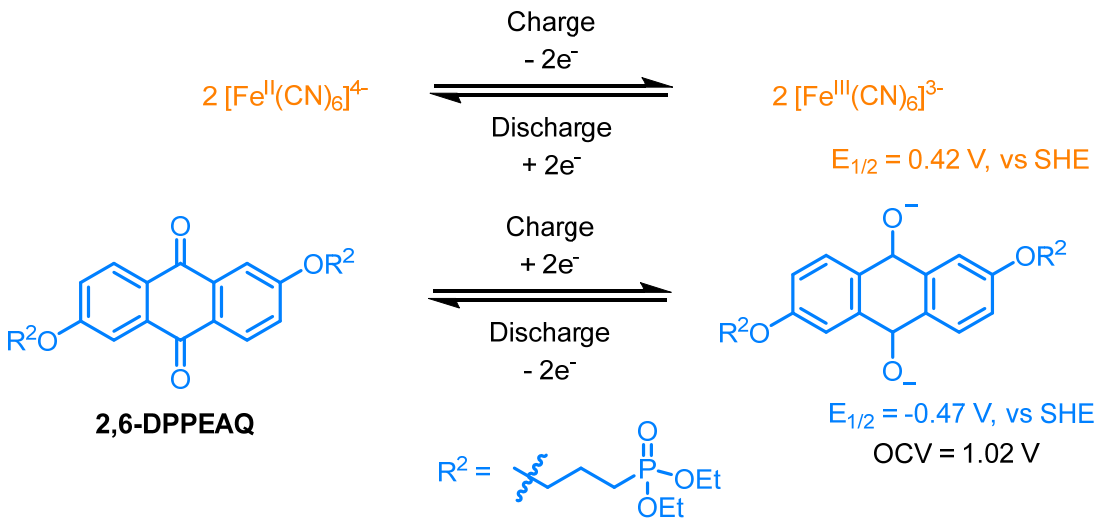
100 mA/cm^2

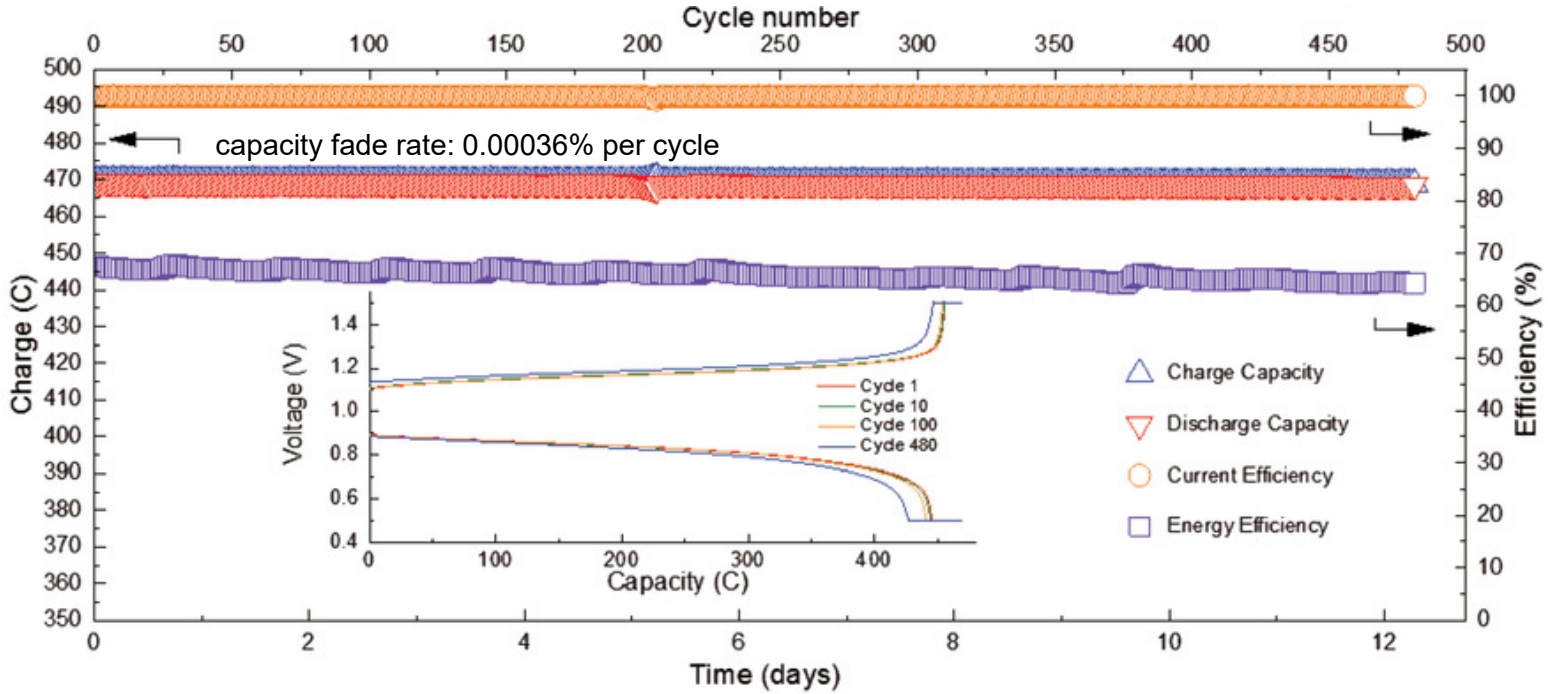
(+) : 30 mL of 0.3 M $K_4[Fe(CN)_6]$ and 0.1 M $K_3[Fe(CN)_6]$

(-): 5 mL of 0.5 M 2,6-DBEAQ at pH 12.

Fumasep E-620 (K) membrane.

Alkaline AORFBs : pH = 9

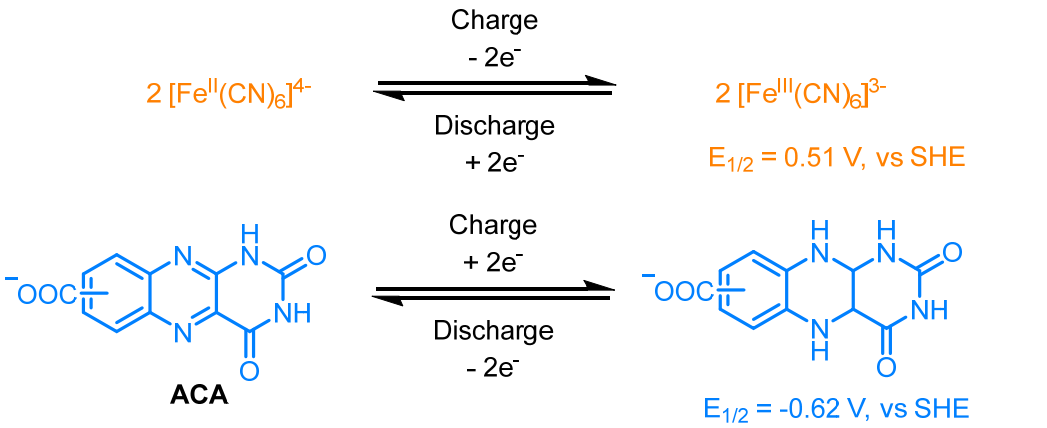


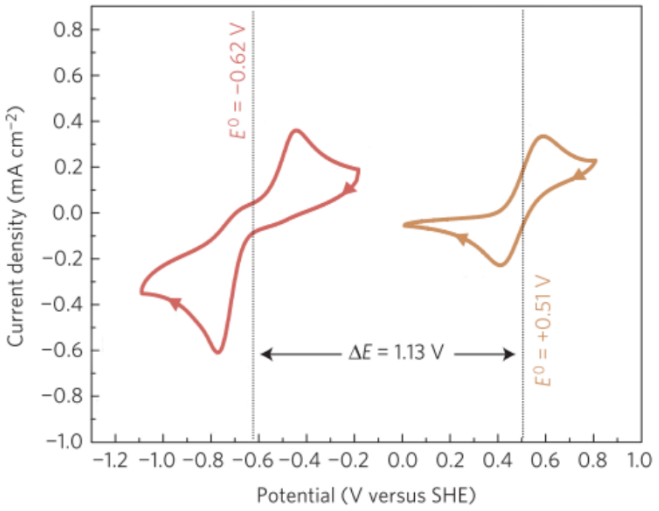


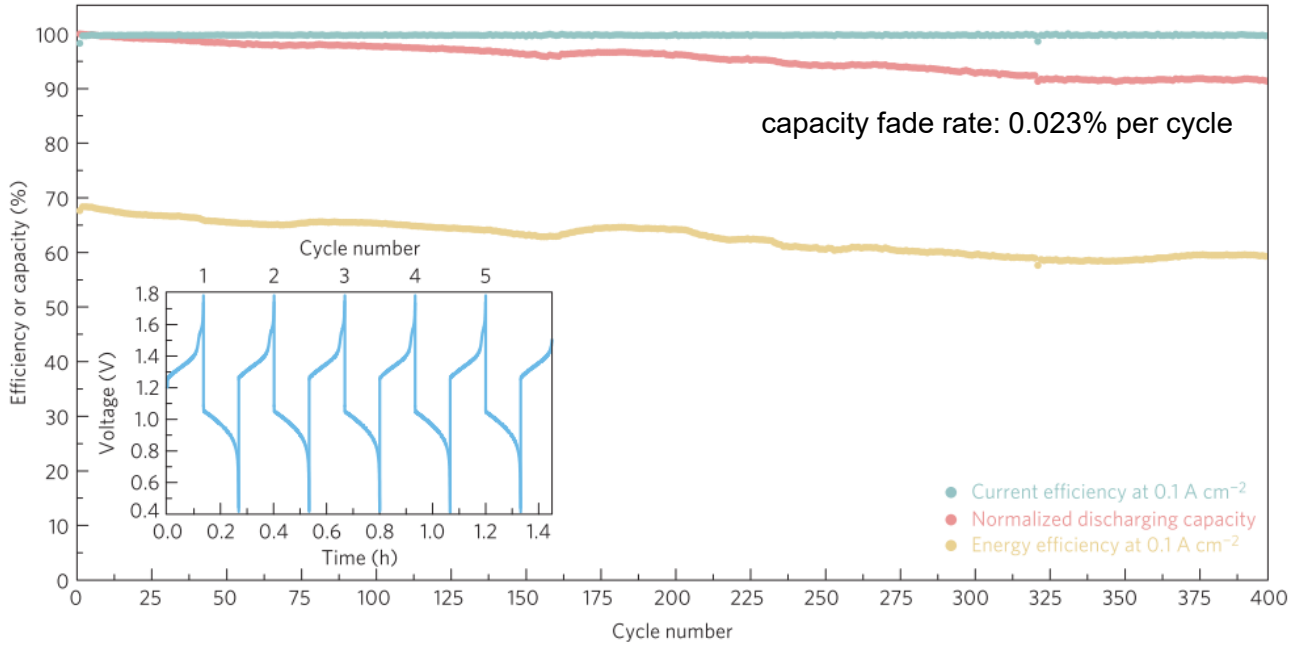
20 mA/cm^2
(+): 40 mL 0.1 M $K_4[Fe(CN)_6]$ and 0.01 M $K_3[Fe(CN)_6]$, 1 M KCl; pH=9
(-): 6.5 mL 0.1 M 2,6-DPPEAQ, 1 m KCl; pH=9
Fumasep E-620 (K)

Gordon, R. G.; Aziz, M. J. et al. *Adv. Energy Mater.* **2019**, *9*, 1900039

Alkaline AORFBs : pH = 14



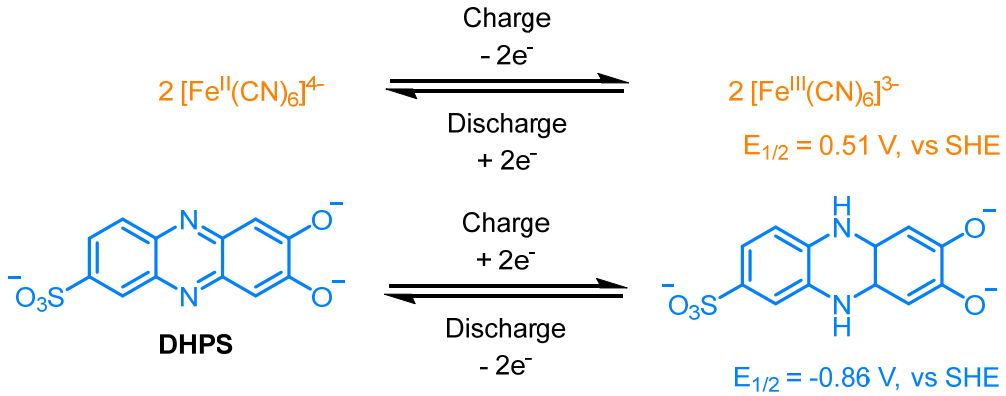




100 mA/cm^2
(+): 0.3 M $K_4[Fe(CN)_6]$, 0.1 M $K_3[Fe(CN)_6]$, 1 M KOH
(-): 0.4 M ACA, 2.5 M KOH
Nafion 212

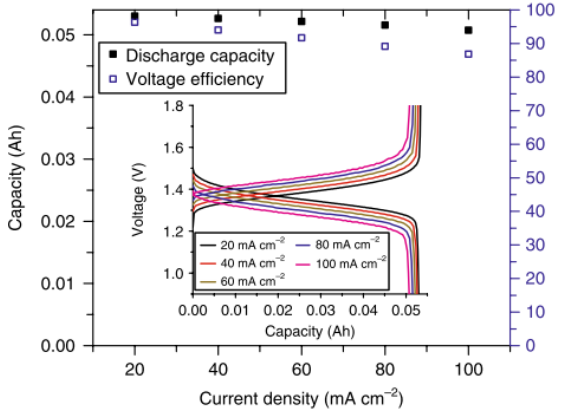
Aziz, M. J.; Gordon, R. G et al. *Nat. Energy* **2016**, *1*, 16102

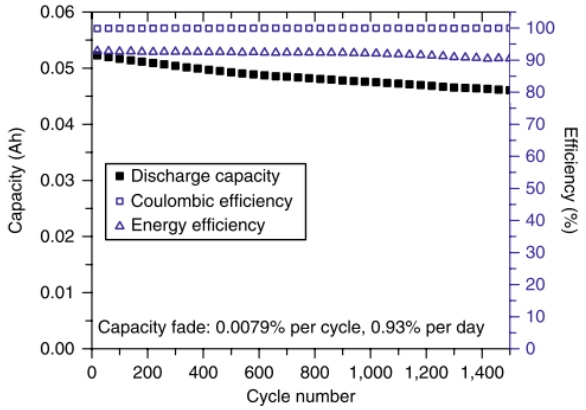
Alkaline AORFBs : pH = 14



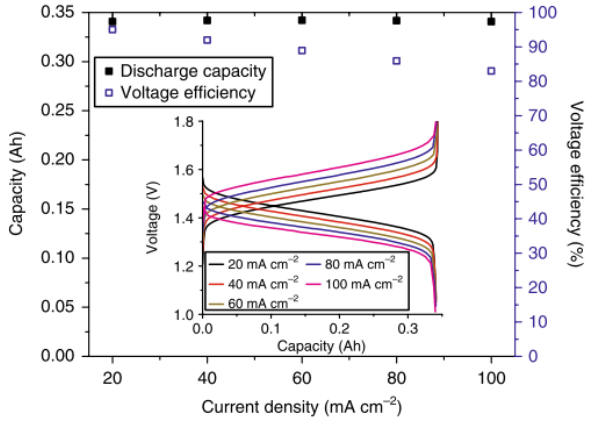
DHPS

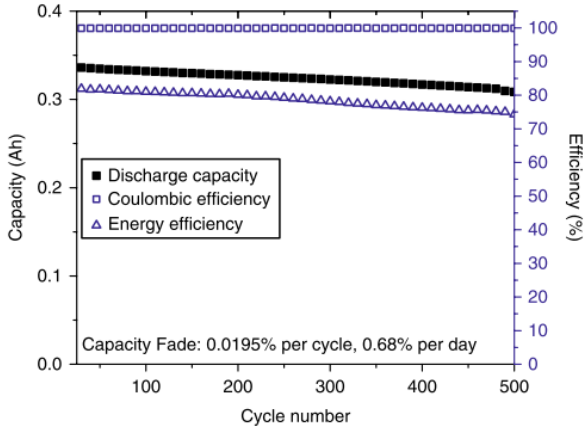
OCV = 1.45 V





50 mA/cm^2
(+): 0.133 M $K_4Fe(CN)_6$/0.067 M $K_3Fe(CN)_6$ dissolved in 15 ml of 1 M NaOH
(-): 10 ml 0.1 M DHPS, 1 M NaOH
Nafion 212

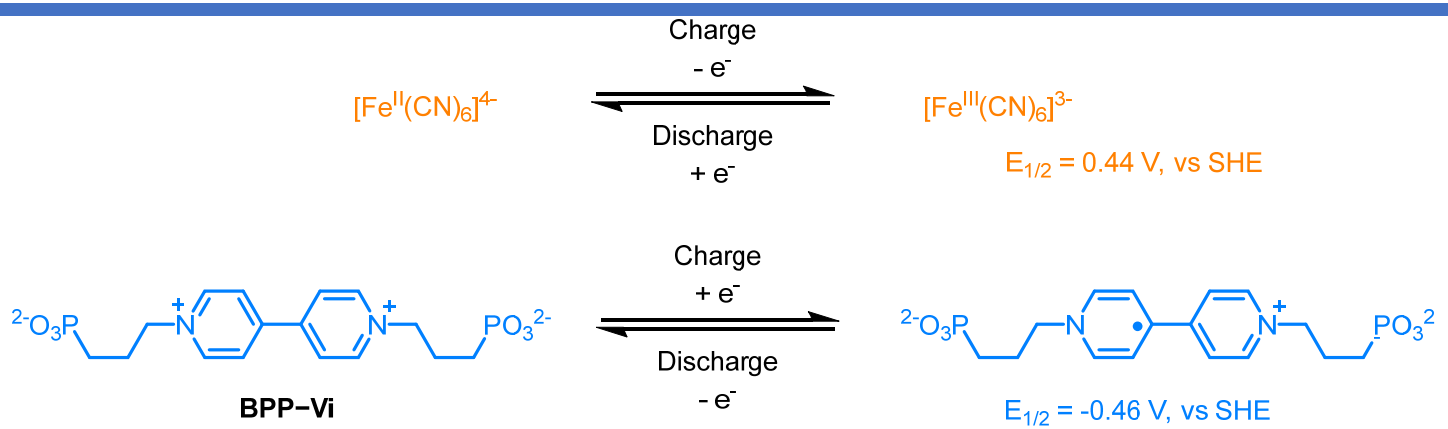




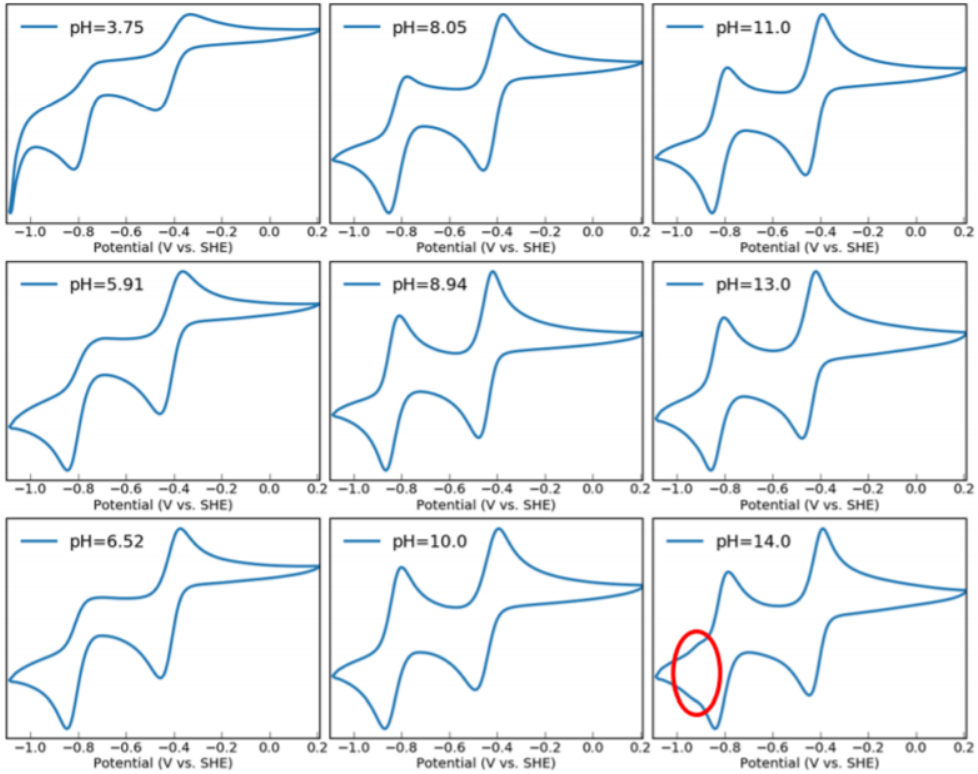
100 mA/cm^2
(+): 0.31 M $K_4Fe(CN)_6$/0.31 M $K_3Fe(CN)_6$ dissolved in 45 ml of 2 M NaOH
(-): 5 ml 1.4 M DHPS, 1 M NaOH
Nafion 212

Wang, W et al. *Nat. Energy* **2018**, *3*, 508

Alkaline AORFBs : pH = 9

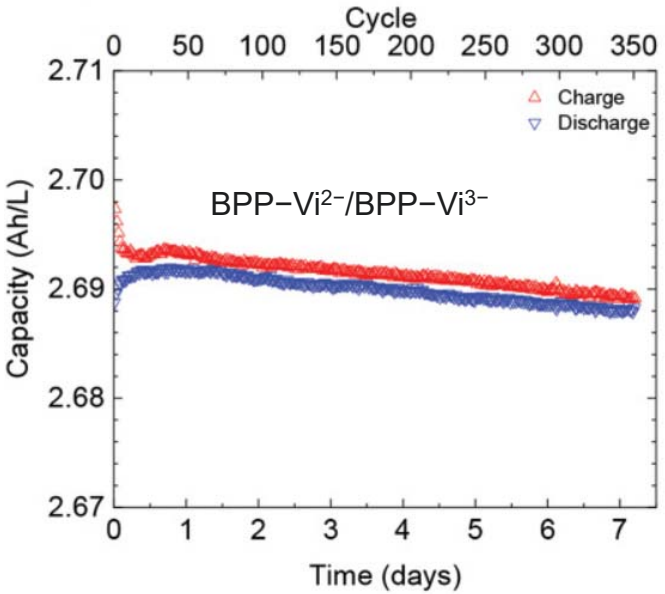


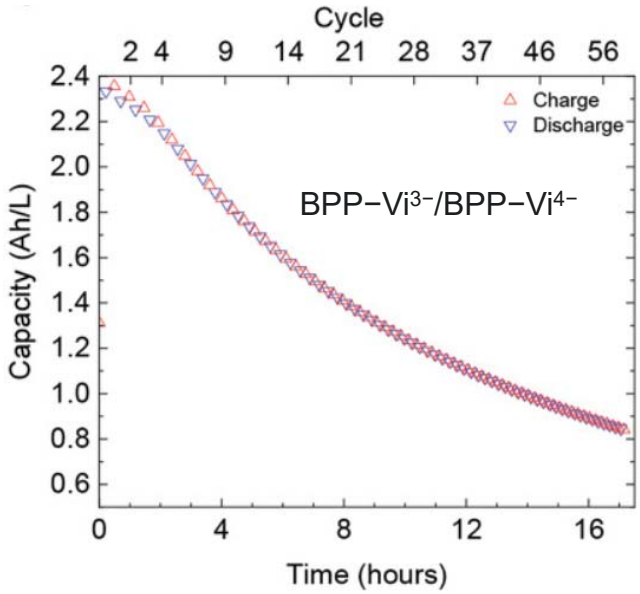
OCV = 0.9 V

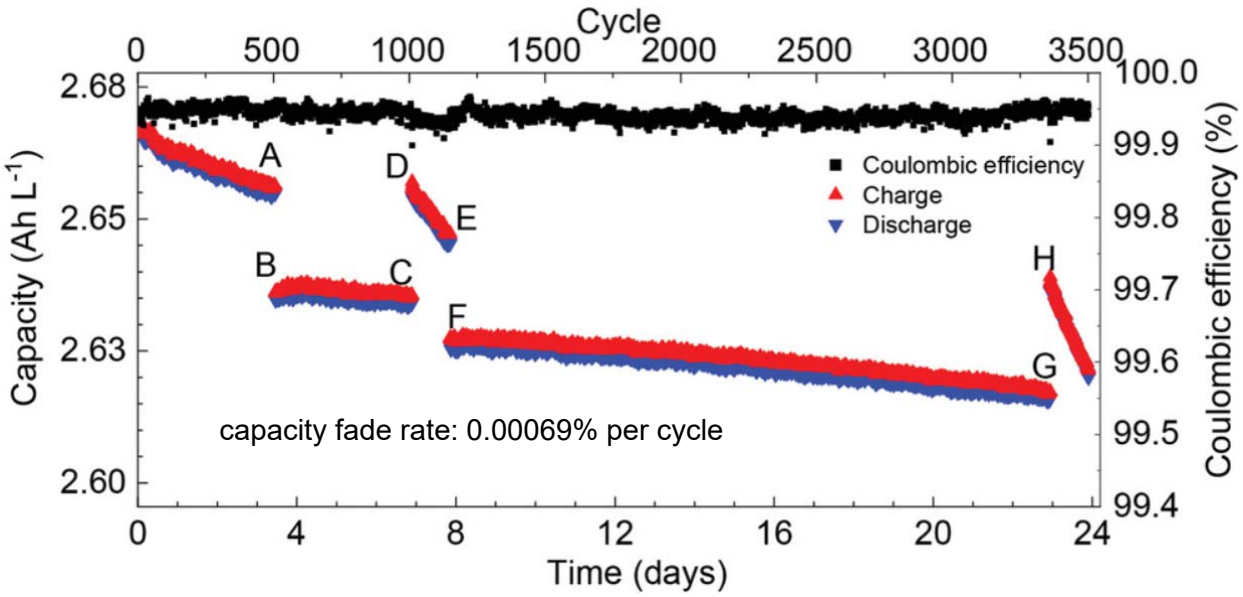


Gordon, R. G.; Aziz, M. J et al. *Adv. Energy Mater.* **2020**, *10*, 2000100

Alkaline AORFBs : pH = 9







40 mA/cm^2
(+): 20 mL of 0.1 M $K_4Fe(CN)_6$ and 0.1 M $K_3Fe(CN)_6$ in 1 M KCl; pH=9
(-): 6.2 mL of 0.1 M BPP−Vi titrated with 1 M KOH in 1 M KCl; pH=9
Fumasep E620(K)

Gordon, R. G.; Aziz, M. J et al. *Adv. Energy Mater.* **2020**, *10*, 2000100

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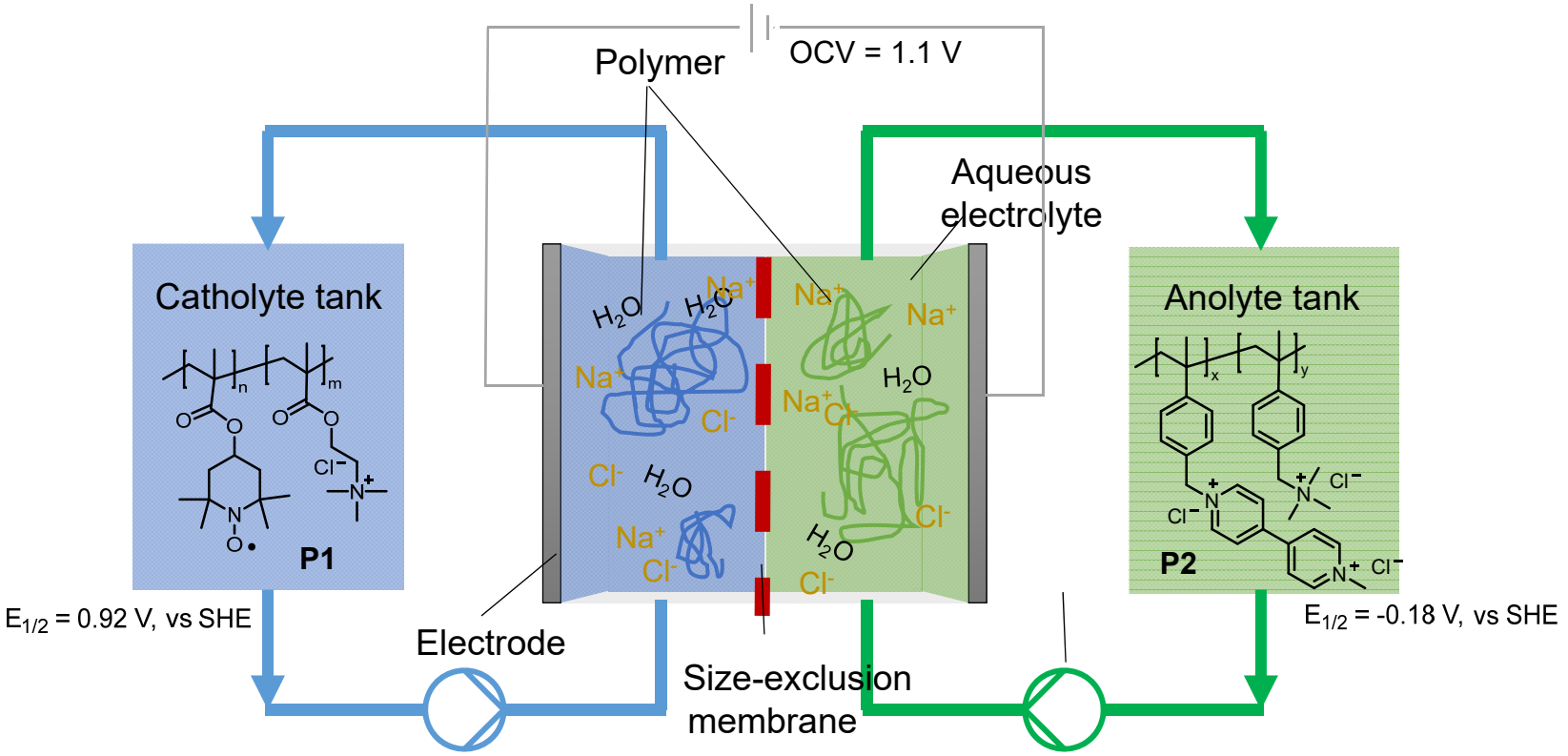
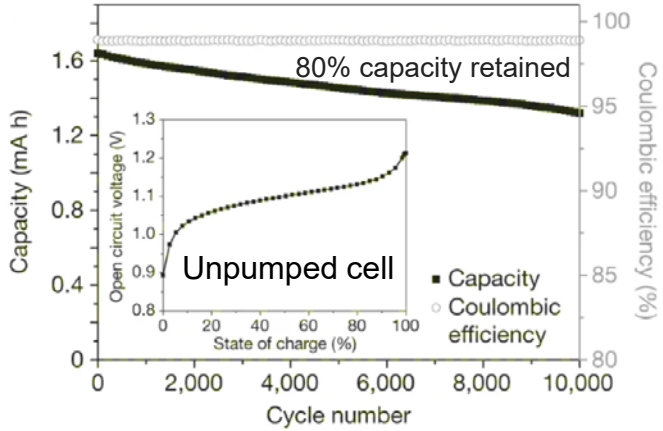
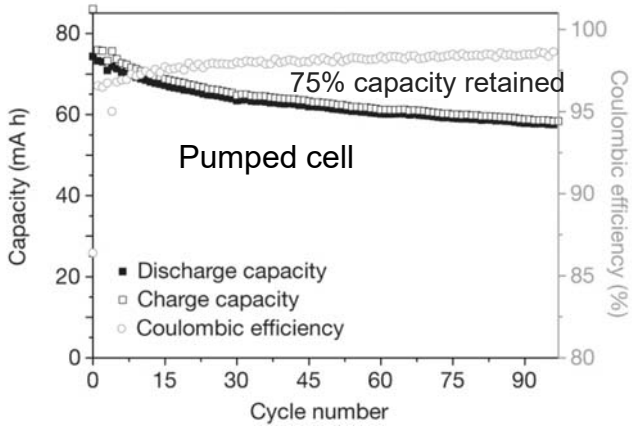
pH Neutral AORFBs



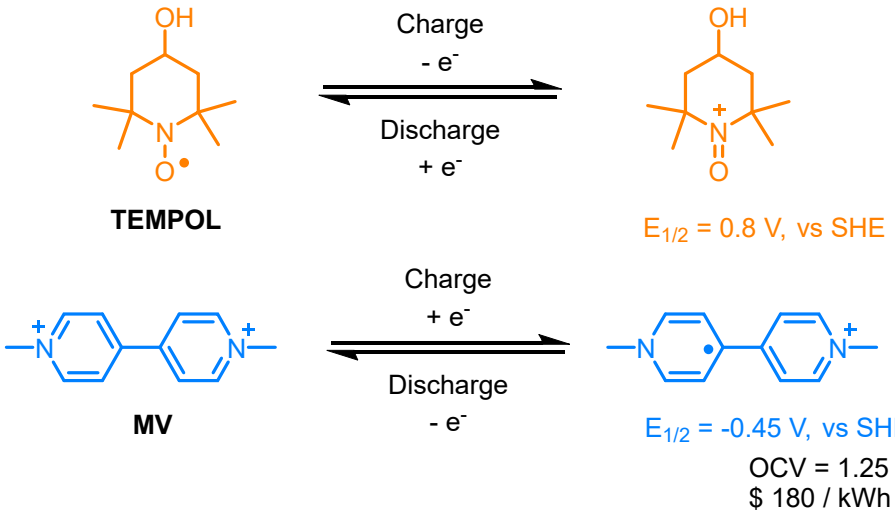


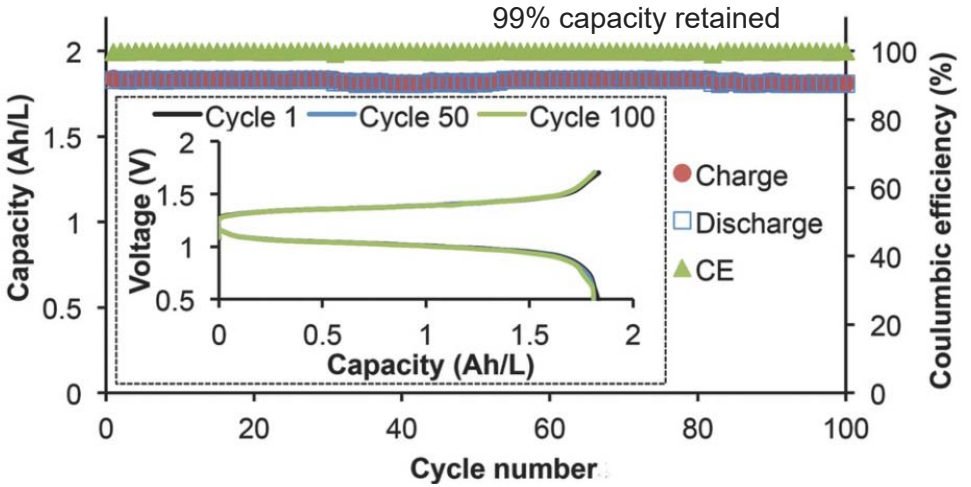


40 mA/cm^2
(+): 10 ml of **P1**, 2 M NaCl
(-): 15 ml of **P2**, 2 M NaCl
cellulose-based dialysis membrane

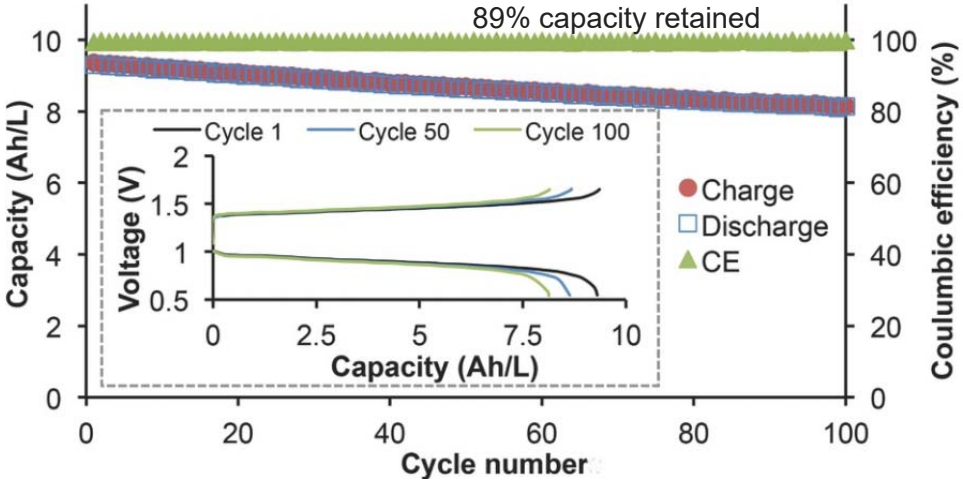
Schubert, U. S et al. *Nature* **2015**, *527*, 78

pH Neutral AORFBs





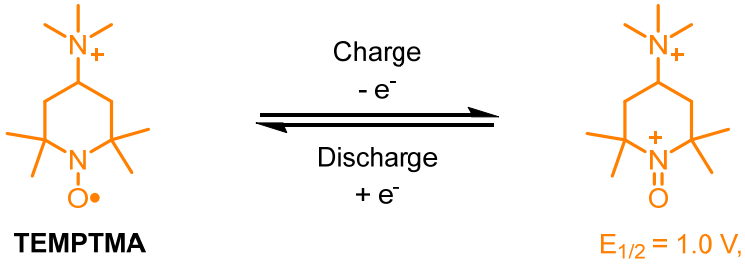
40 mA/cm^2; (+): 0.1 M 4-HO-TEMPO in 1.0 M NaCl;
(-): 0.1 M MV in 1.0 M NaCl; Selemion (120μm)



60 mA/cm^2; (+): 0.5 M 4-HO-TEMPO in 1.5 M NaCl;
(-): 0.5 M MV in 1.5 M NaCl; Selemion (120μm)

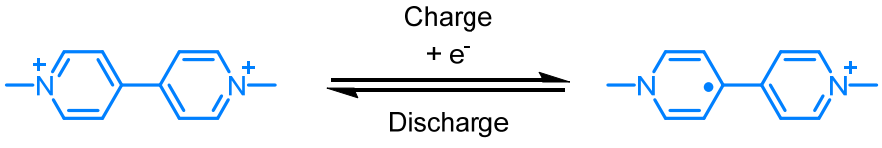
Liu, T.; Wang, W et al. *Adv. Energy Mater.* **2016**, *6*, 1501449

pH Neutral AORFBs



TEMPTMA

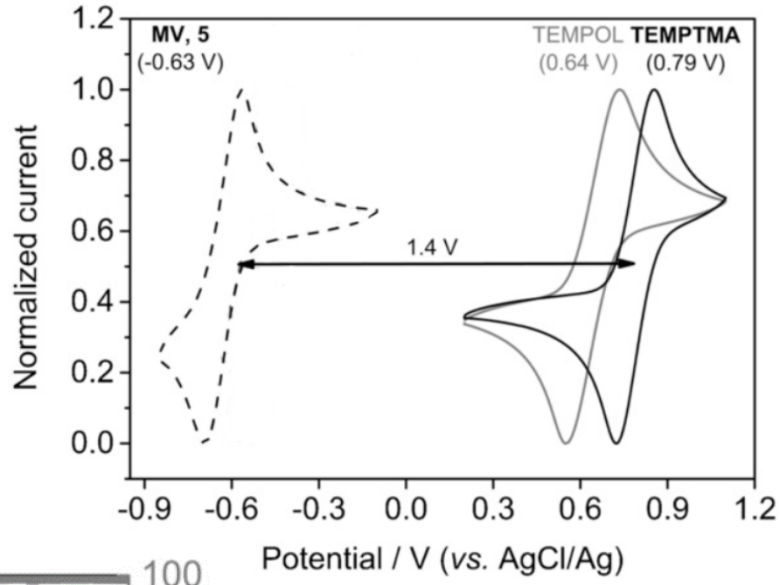
$E_{1/2}$ = 1.0 V, vs SHE

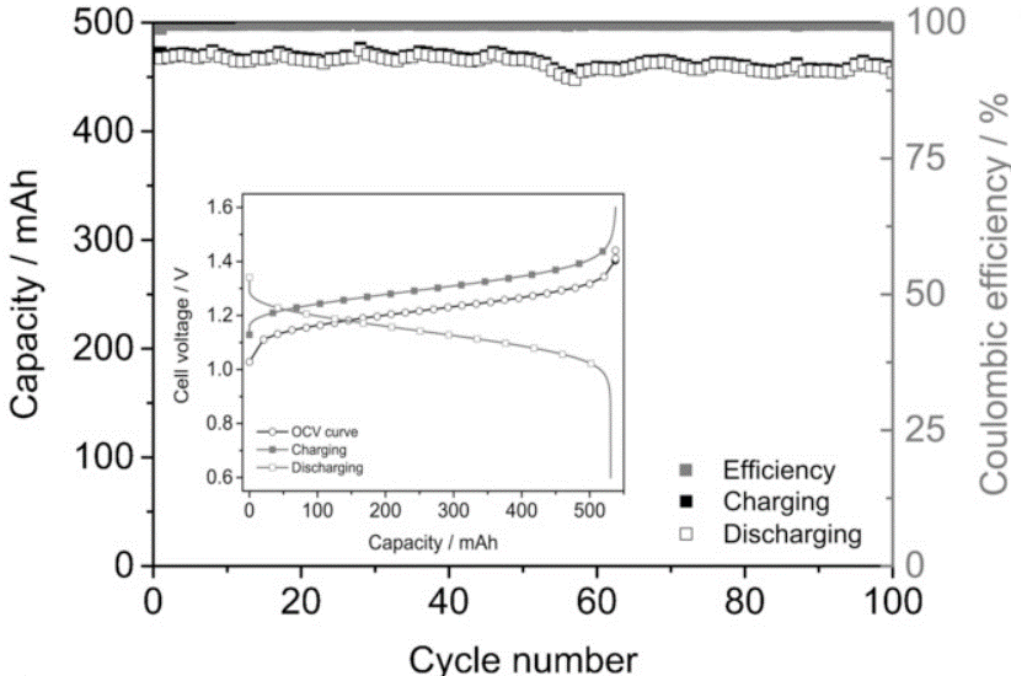


MV

$E_{1/2}$ = -0.45 V, vs SHE

OCV = 1.35 V

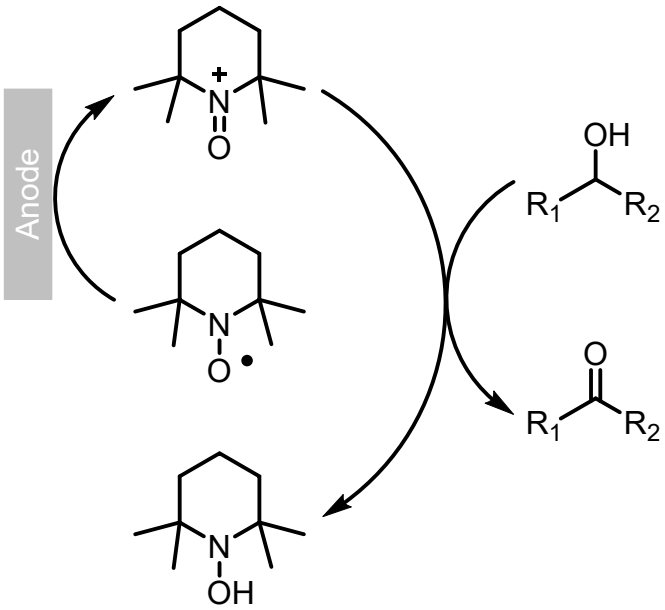


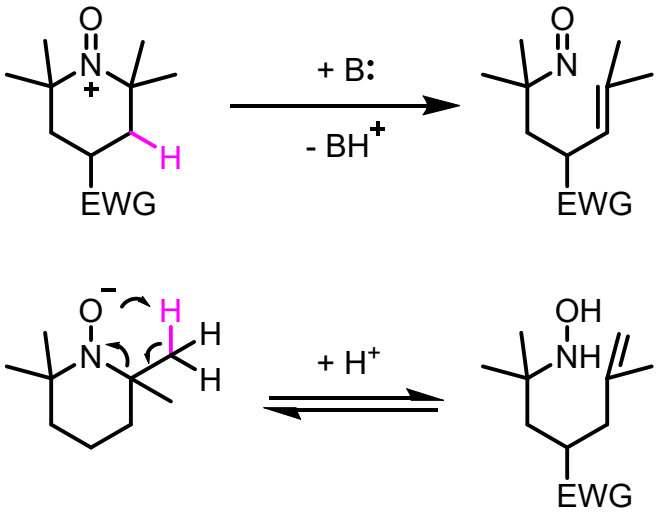


80 mA/cm^2
(+): 12mL of 2.0 M TEMPTMA
(-): 12mL of 2.0 M MV
fumasep FAA-3-PE-30

Schubert, U. S et al. *Angew. Chem. Int. Ed.* **2016**, *55*, 14427

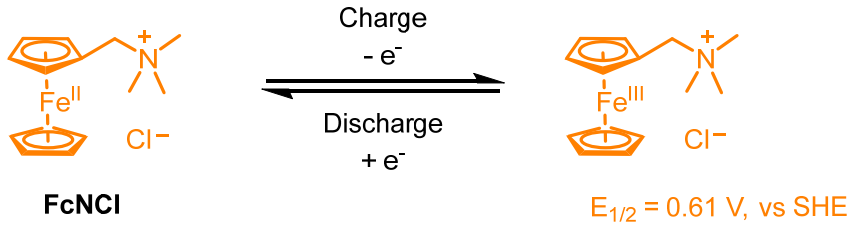
pH Neutral AORFBs





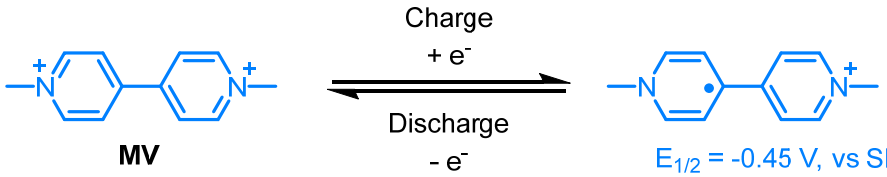
Malinski, T. et al. *J. Phys. Chem.* **1988**, *92*, 3745
Braslau, R. et al. *J. Polym. Sci. A Polym. Chem.* **2006**, *44*, 697

pH Neutral AORFBs



FcNCl

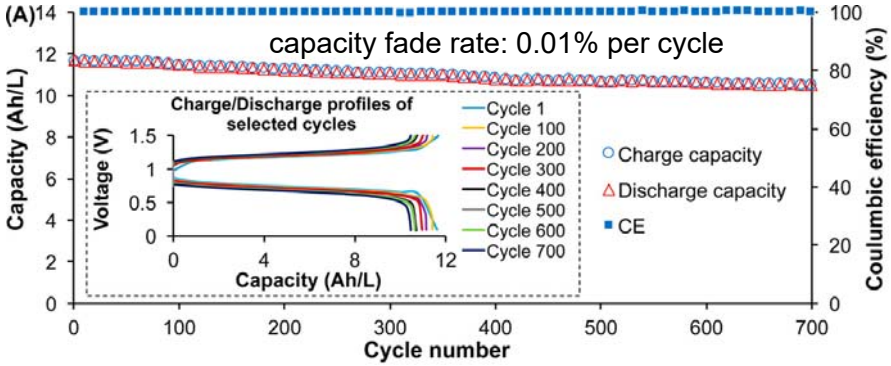
$E_{1/2}$ = 0.61 V, vs SHE



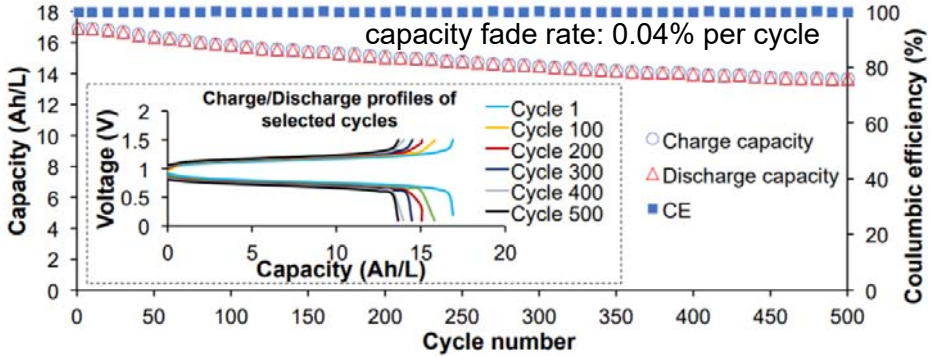
MV

$E_{1/2}$ = -0.45 V, vs SHE

OCV = 1.0 V
$ 2 / kg
~ $ 162 / kWh (total)



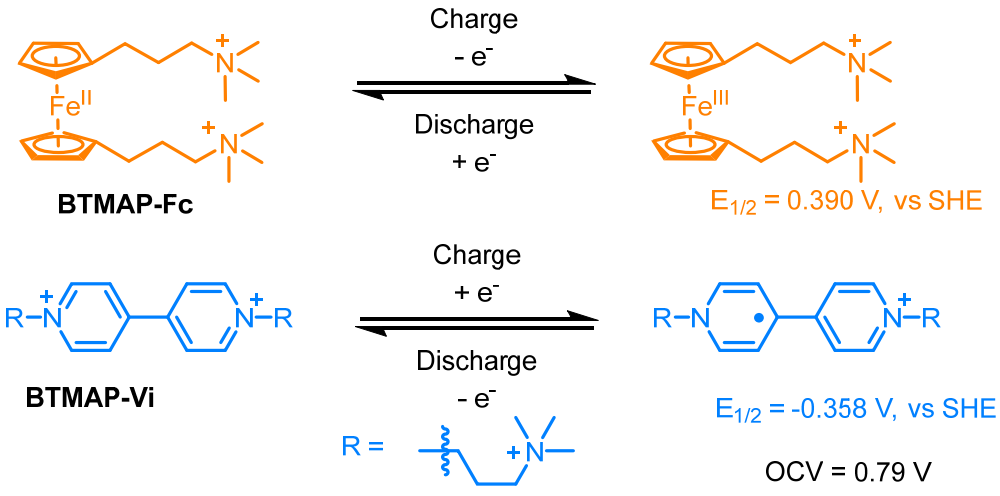
60 mA/cm^2
(+): 0.5 M FcNCl in 2.0 M NaCl
(-): 0.5 M MV in 2.0 M NaCl
Selemion AMV

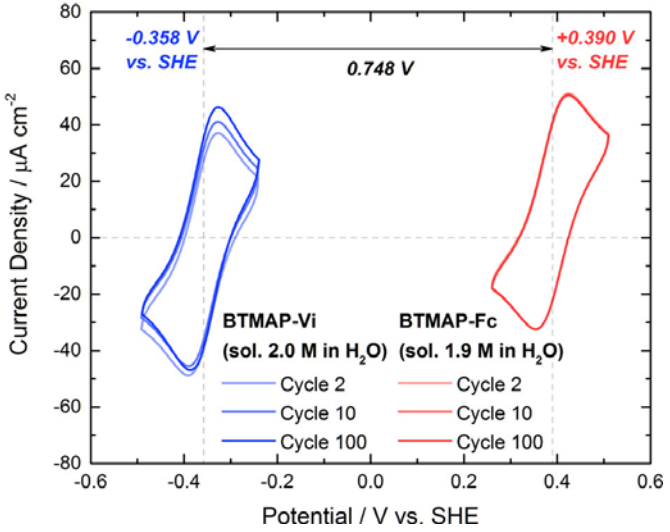


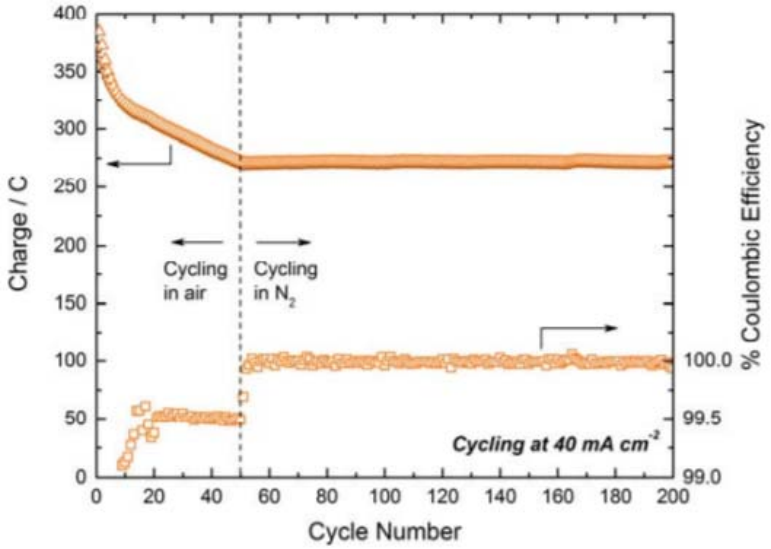
60 mA/cm^2
(+): 0.7 M FcNCl in 2.0 M NaCl
(-): 0.7 M MV in 2.0 M NaCl
Selemion AMV

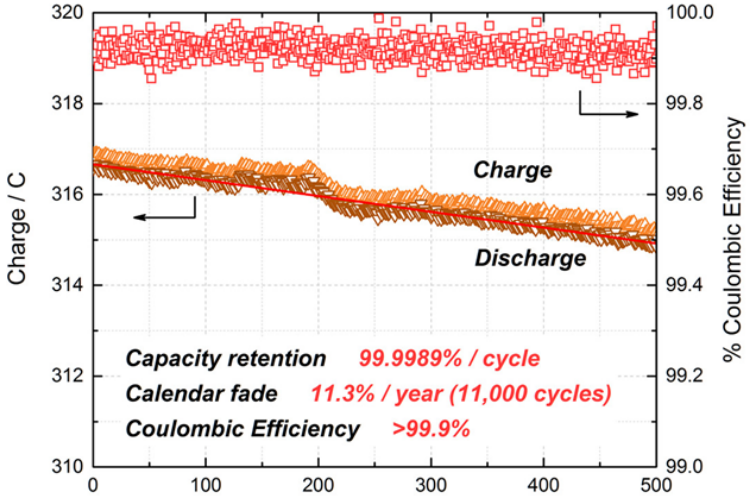
Liu, T. L et al. *J. Am. Chem. Soc.* **2017**, *139*, 1207

pH Neutral AORFBs









50 mA/cm²

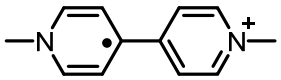
(+): 3.25 mL of 1.00 M BTMAP-Fc

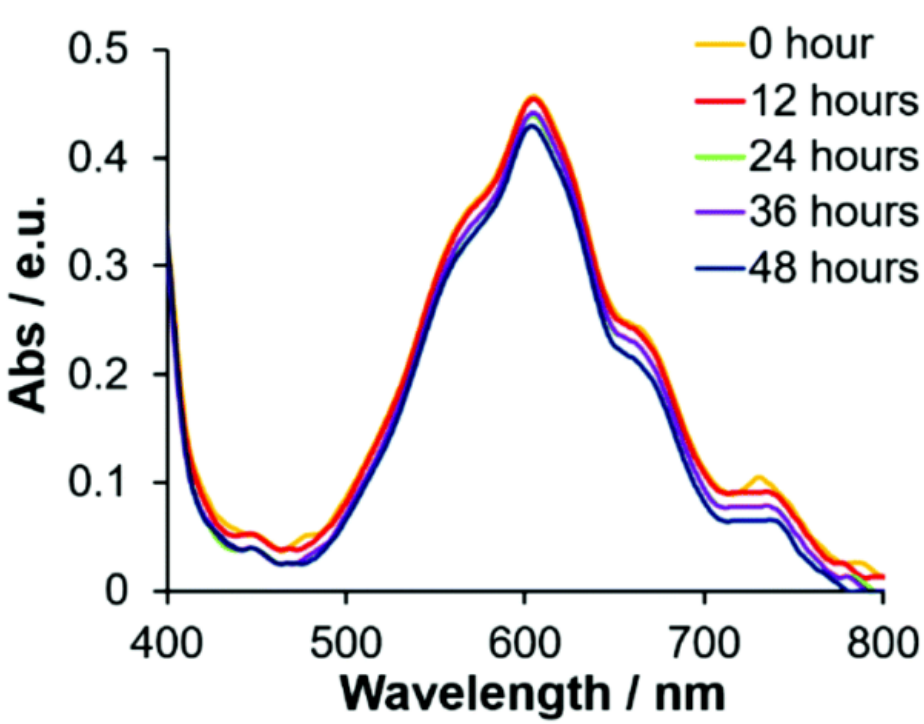
(-): 7.50 mL of 0.75 M BTMAP-Vi

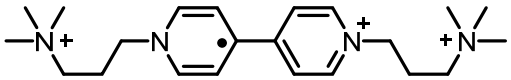
Selemion DSV

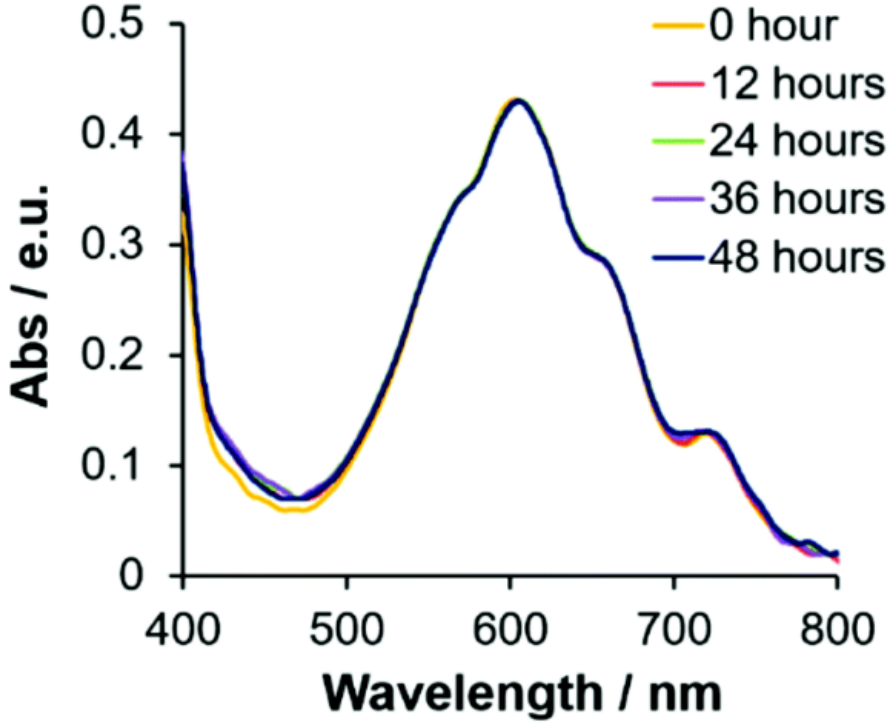
Gordon, R. G.; Aziz, M. J et al. *ACS Energy Lett.* **2017**, *2*, 639

pH Neutral AORFBs



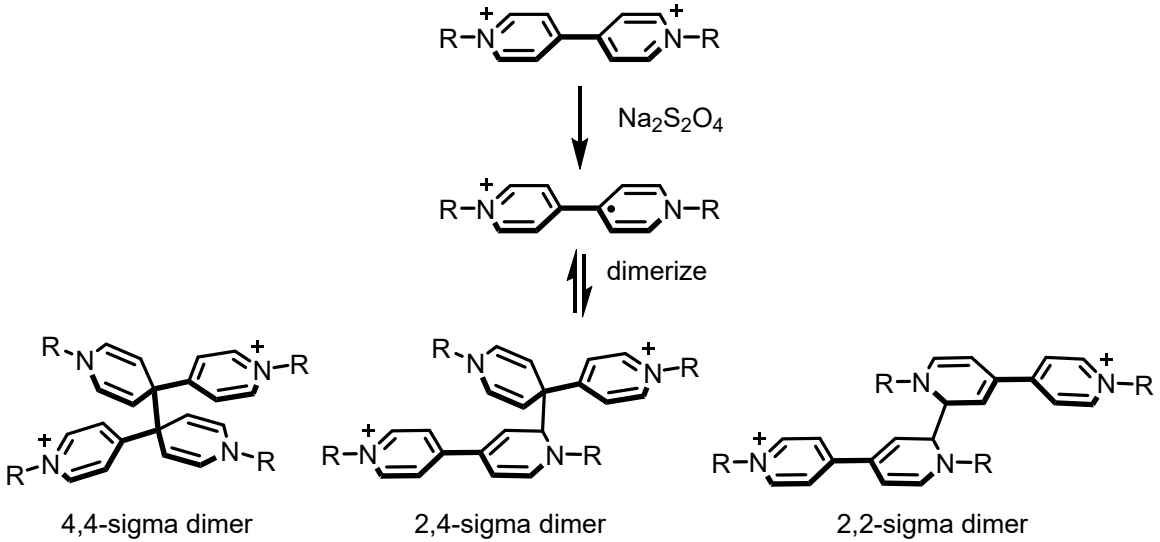


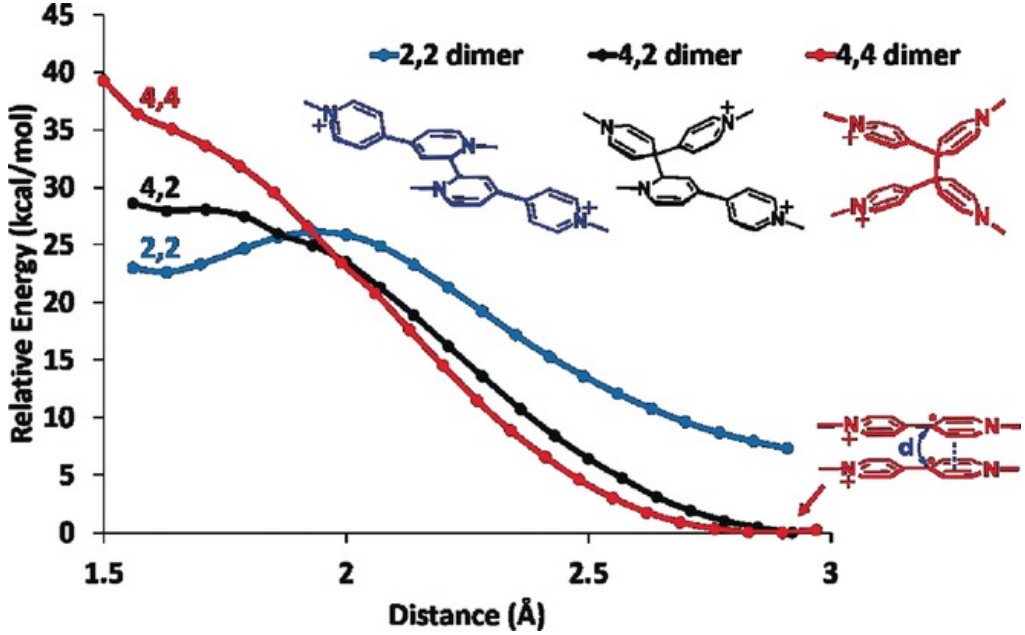




Liu, T. L et al. *Chem. Commun.* **2018**, *54*, 6871

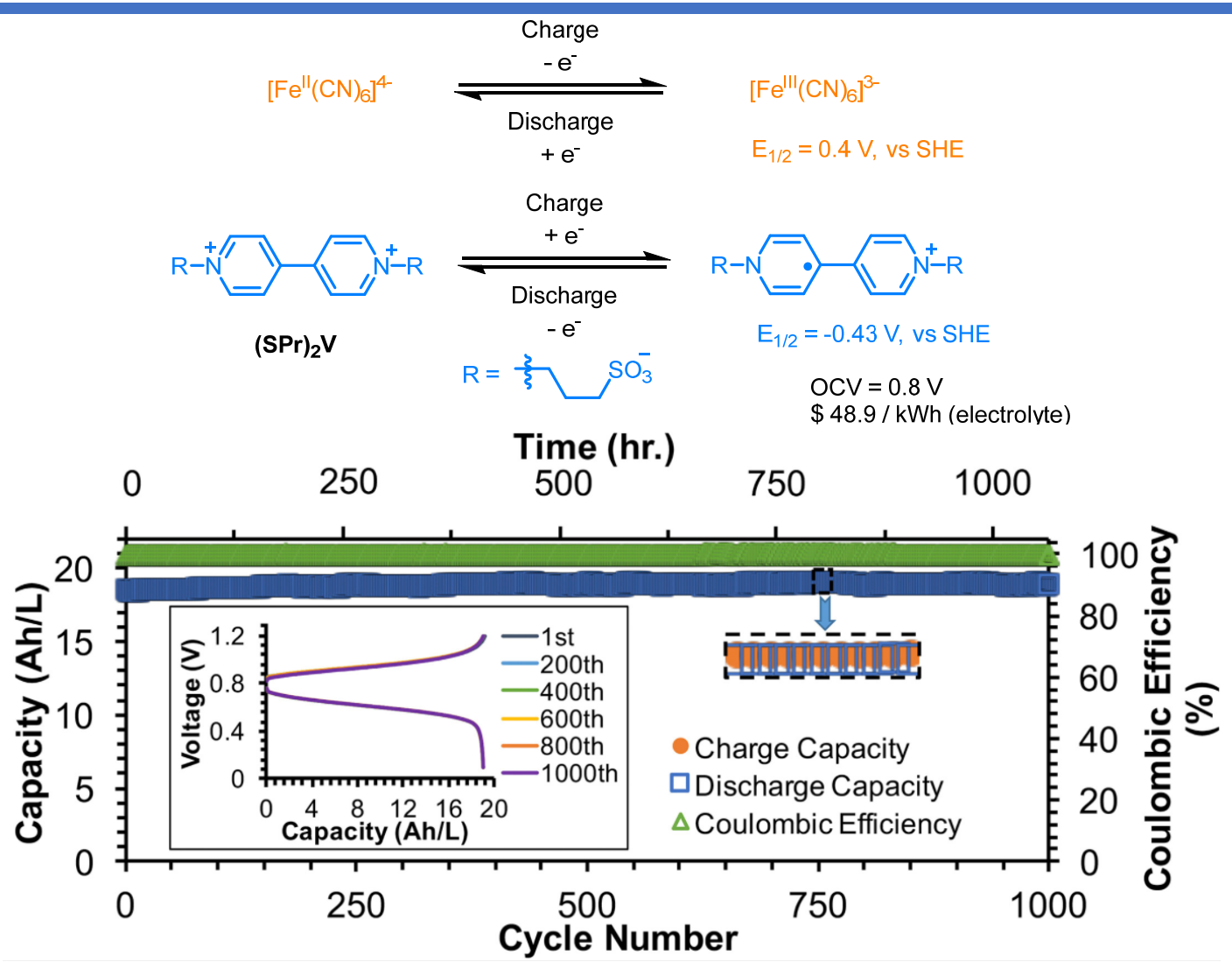
pH Neutral AORFBs





Winter, A. H et al. *Angew. Chem. Int. Ed.* **2017**, *56*, 9435

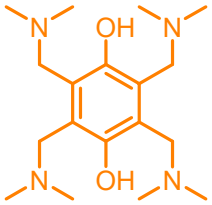
pH Neutral AORFBs



40 mA/cm^2; (+), (-) : 0.9 M $(NH_4)_4[Fe(CN)_6]$ + 0.9 M $(SPr)_2V$; Selemion CSO
EE: 62.6%
pH values of the electrolytes were adjusted to 7.0 using a diluted $NH_3 \cdot H_2O$ or HCl solution.

Liu, T. L et al. *Joule* **2019**, *3*, 149

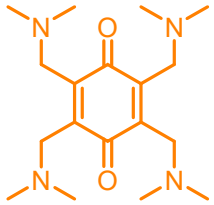
pH = 14.6 | pH = -0.7



FQH_2

Charge
- 2e⁻

Discharge
+ 2e⁻



FQ

\+ $2H^+$

$E_{1/2}$ = 0.7 V, vs SHE

$Zn(OH)_4^{2-}$

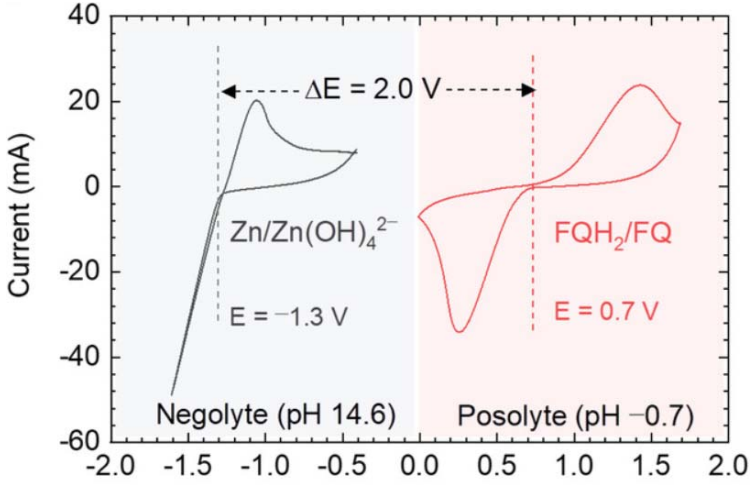
Charge
+ 2e⁻

Discharge
- 2e⁻

Zn + $4OH^-$

$E_{1/2}$ = -1.3 V, vs SHE

OCV = 1.99 V

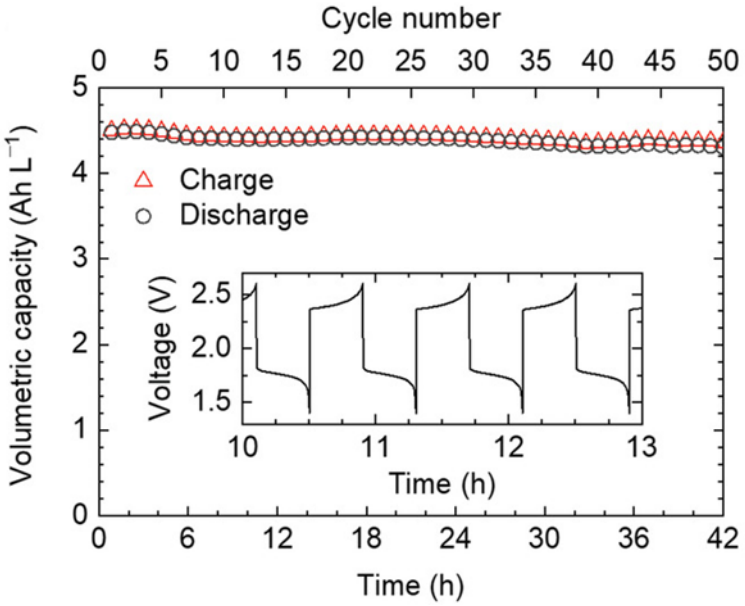


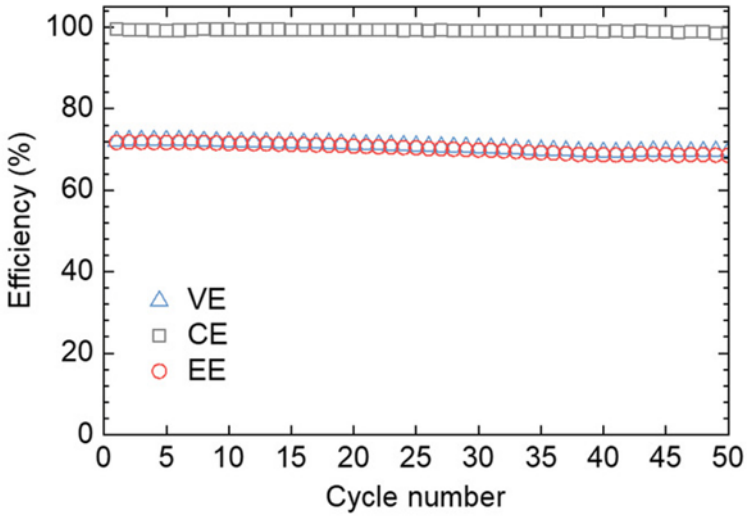
20 mA/cm²

(+): 0.1 M FQH_2, 2.5 M sulfuric acid

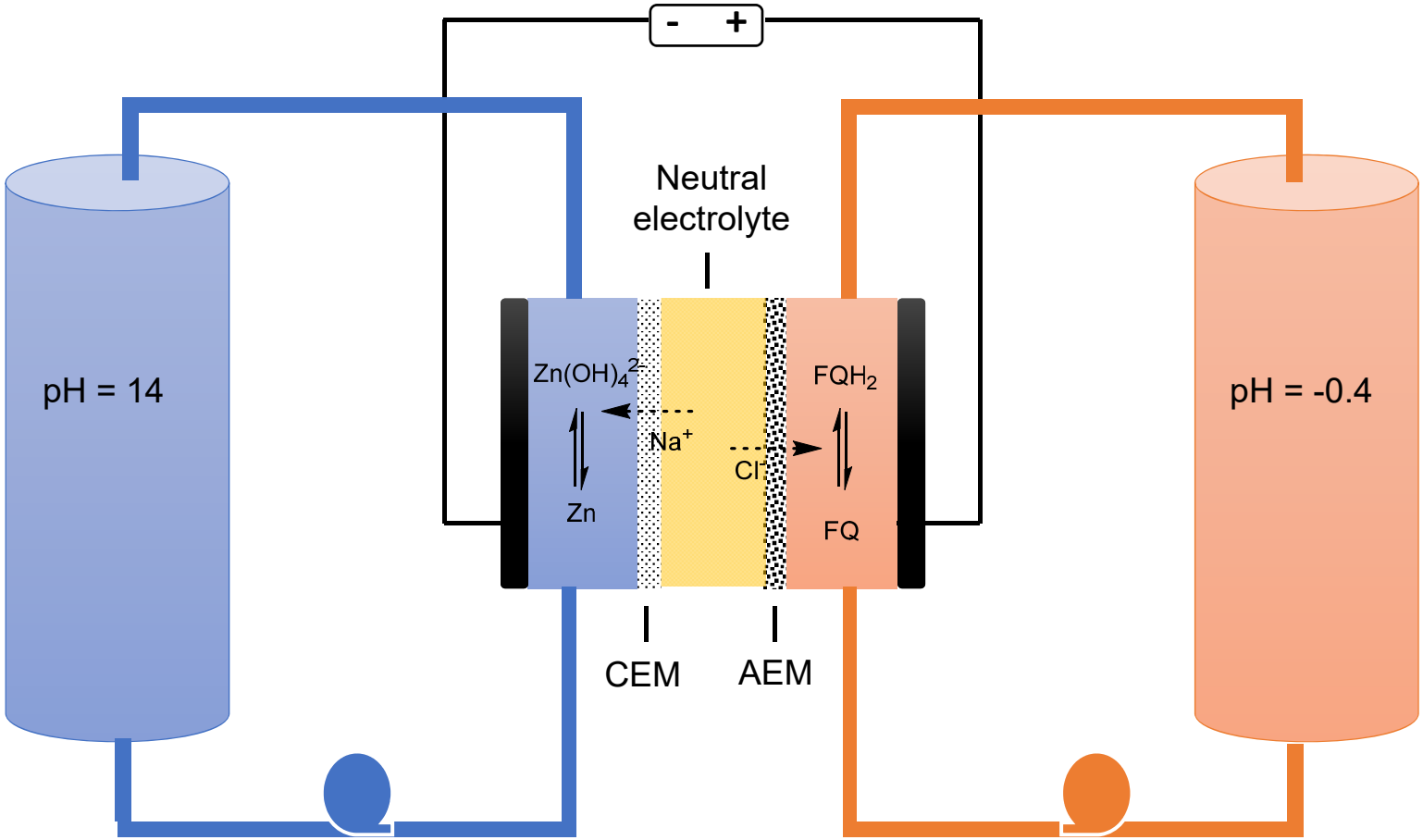
(-): ZnO + 4 M NaOH to reach 2 M $[Zn(OH)_4]^{2-}$

Nafion 117 as CEM; Selemion DSV as AEM





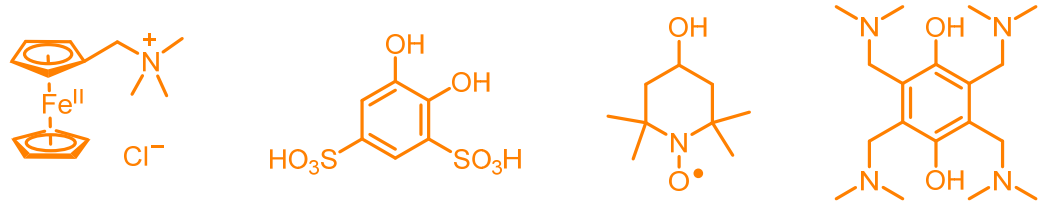
Cho, J.; Aziz, M. J et al. *Adv. Energy Mater.* **2019**, *9*, 1900694


-
+
Neutral
electrolyte
pH = 14
pH = -0.4
$Zn(OH)_4^{2-}$
Na^+
Cl^-
FQH_2
Zn
FQ
CEM
AEM

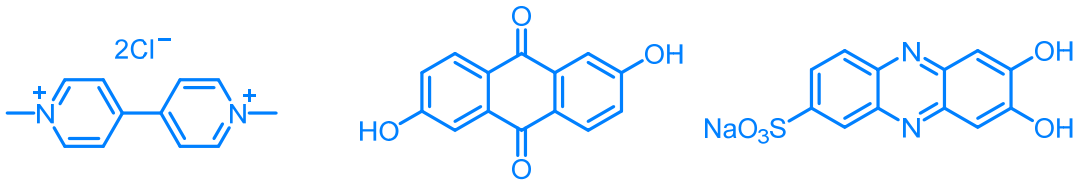
1. Background and Brief Introduction
2. Types of AORFBs
    I. Acidic AORFBs
    II. Alkaline AORFBs
    III. pH Neutral AORFBs
3. Summary and Outlook

Summary

Anolyte molecules



Catholyte molecules



Advantages:

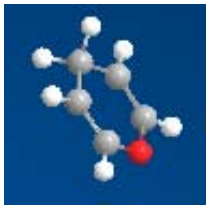
- Safe
- Inexpensive
- More Electrons
- High conductivity
- Well-developed membranes

Disadvantages:

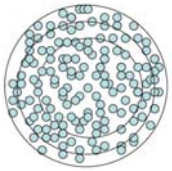
- Limited voltage
- Solubility
- Stability

Outlook

- Molecules with different structure



- High concentration



- Stable for years

- Further research on potentiostatic cycling

Thanks for your attention!