Azoniafluorenone-based Compounds as Two-electron Storage Electrolytes for pH-Neutral Aqueous Organic Redox Flow Batteries

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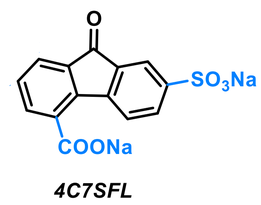
INTRODUCTION

Fluorenones have been developed as suitable candidates for negolytes in Aqueous Organic Flow Batteries (AOFBs). They are water soluble and can store two electrons, coupled with a high stability achieved with the appropriate molecular design. In previous works, Wang (2021) [1] and Fu (2023) [2] studied the performance of some fluorenone-derivatives as negolytes, however some limitations restrain their further application in flow batteries.

In this work, we investigated a new family of azoniafluorenone-based materials that allow storing two-electrons in a neutral-pH electrolyte. We successfully developed a general synthetic pathway to make a wide range of azoniafluorenone compounds in a versatile, scalable and efficient way. The most promising material have already demonstrated high energy density and stability when tested in lab-scale flow cells.

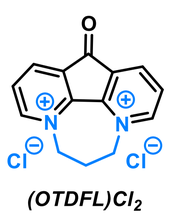
Wang (2021)



4C7SFL

- *very high stability*
- *alkaline media*
- *limited scope for modifications*

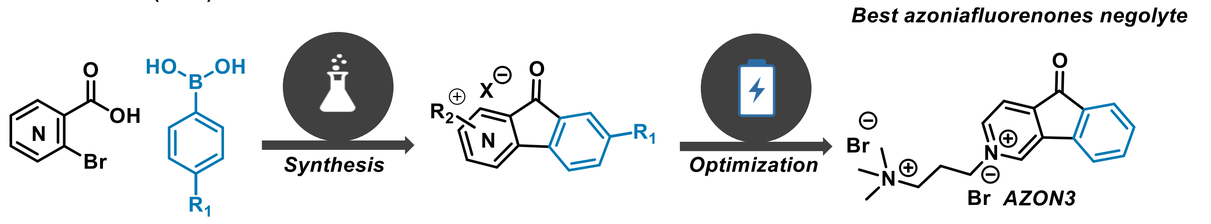
Fu (2023)



(OTDFL)Cl$_2$

- *low stability*
- *neutral media*
- *limited scope for modifications*

This Work (2024)



- *inexpensive*
- *commercially avalaible*
- *platform molecules*
- *new scaffold for AOFBs*
- *high stability and solubilty in batteries*
- *near-neutral media*

[1] R. Feng, X. Zhang, V. Murugesan, A. Hollas, Y. Chen, Y. Shao, E. Walter, N. P. N. Wellala, L. Yan, K. M. Rosso, W. Wang, *Science* (2021), *372*, 836.

[2] W. Li, J. Li, X. Yuan, Z. Xiang, Z. Liang, Z. Fu, *Journal of Materials Chemistry A* (2023), *11*, 19308

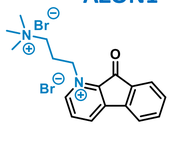
DEVELOPED MATERIALS AND FIRST RESULTS

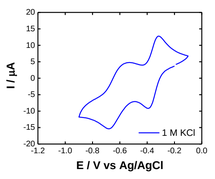
We synthetized azoniafluorenones derivatives considering different substituents and position of the nitrogen on the pyridinium ring, as well as the addition of a substituent on the second ring.

We first studied them via cyclic voltammetry measurements and low concentrated flow cells in 1M KCl (5 mM concentration of AZON).

Different site of N-substitution

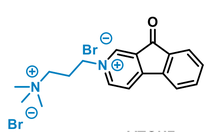
AZON1

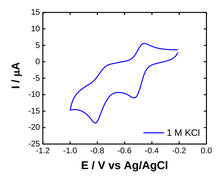




Reversible
High solubility
Low stability in flow-cell

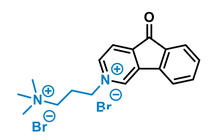
AZON2

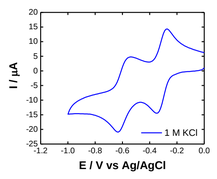




Poorly-reversible
High solubility

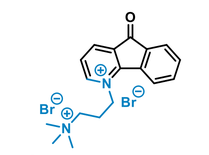
AZON3

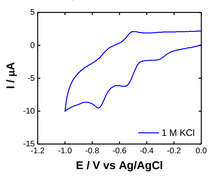




Reversible
High solubility (1.64 M in KCl)
High stability in flow-cell

AZON4

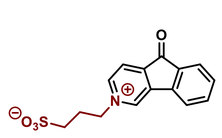


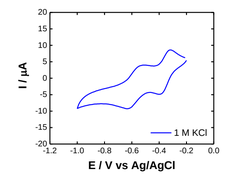


Poorly-reversible
High solubility

Different substituent

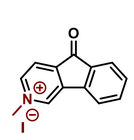
AZONS3

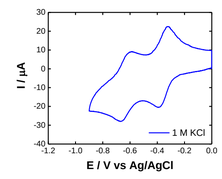




Poorly-reversible
Low solubility (< 5 mM)

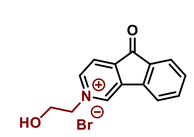
AZONMe3

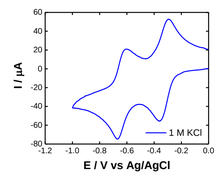




Reversible
Low solubility (< 1 mM)

AZONE3

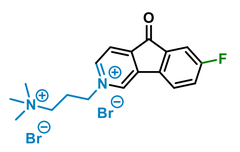


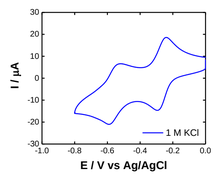


Reversible
High solubility
Low stability in flow-cell

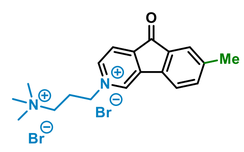
Addition of substituent on second ring

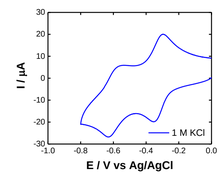
AZON3F





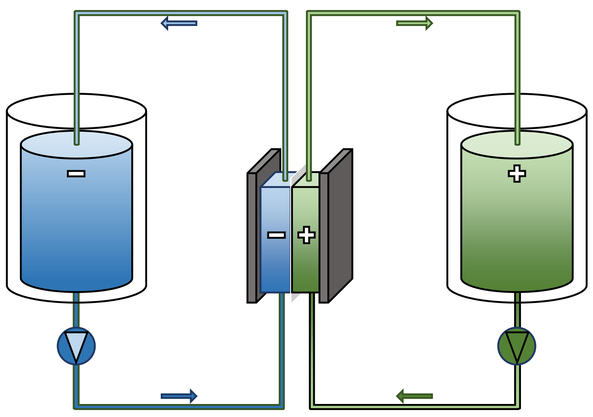
AZON3Me



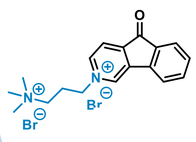


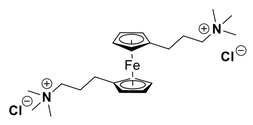
Similar results than AZON3, with AZON3F presenting a slight positive potential shift (electrowithdrawing effect of F)

AZON3 FLOW BATTERY TESTS

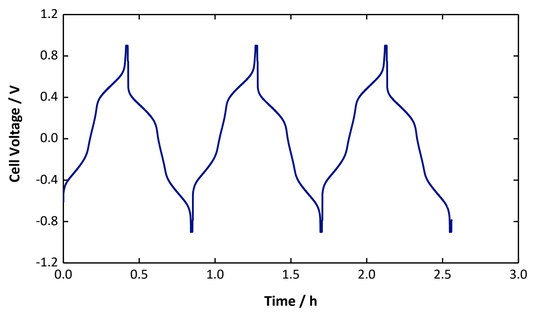


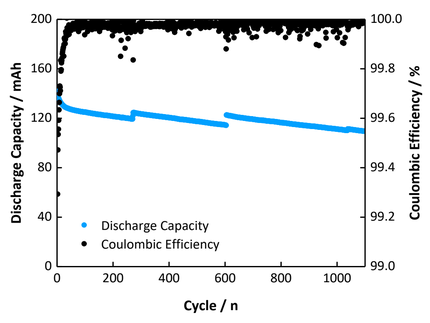
- Supporting Electrolyte: KCl
- Inside N_2-filled GloveBox
- Excess amount of Posolyte
- AEM Selemion DSVN
- CCCV cycling protocol (60 mA cm^{-2})





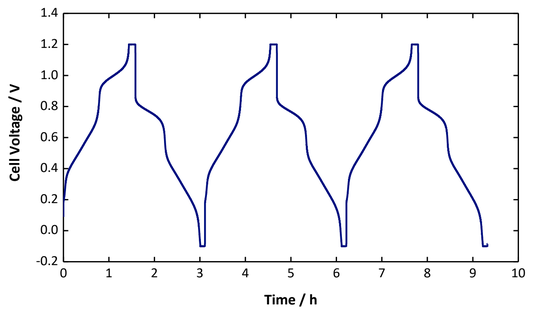
AZON3 0.5M Symmetric Cell

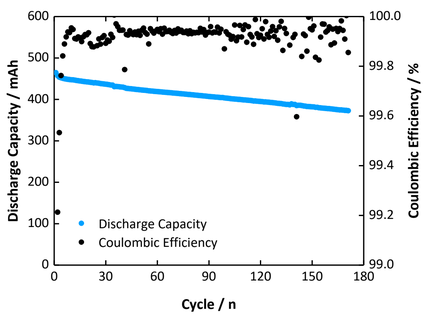




Capacity fade rate
0.010 %/cyc - 0.27 %/day
Coulombic efficiency
99.98 %
Capacity utilization
82 %

AZON3 1M Full Cell





Capacity fade rate
0.097 %/cyc - 0.79 %/day
Coulombic efficiency
99.94 %
Energy efficiency
65.2%
Capacity utilization
87 %
Volumetric capacity
46.4 Ah L^{-1}

CONCLUSIONS

- **Azoniafluorenones presented as AOFBs-negolytes, offering high solubility in aqueous electrolytes and 2-electron storage.**
- **Synthetic route developed for accessing a wide range of azoniafluorenone derivatives with an open scope for further research.**
- **AZON3, including ammonium quaternary group, already demonstrated high performance in near-neutral flow battery at high concentration, with high volumetric capacity and stability for 2-electron-cycling.**