Micellar solubilization for high-energy-density aqueous organic redox flow batteries

Youngsu Kim[a], Giyun Kwon[a], Sung-O Park[a], and Kisuk Kang[a,*]

[a]Department of Materials Science and Engineering, Seoul National University
E-mail address: youngsufous@snu.ac.kr

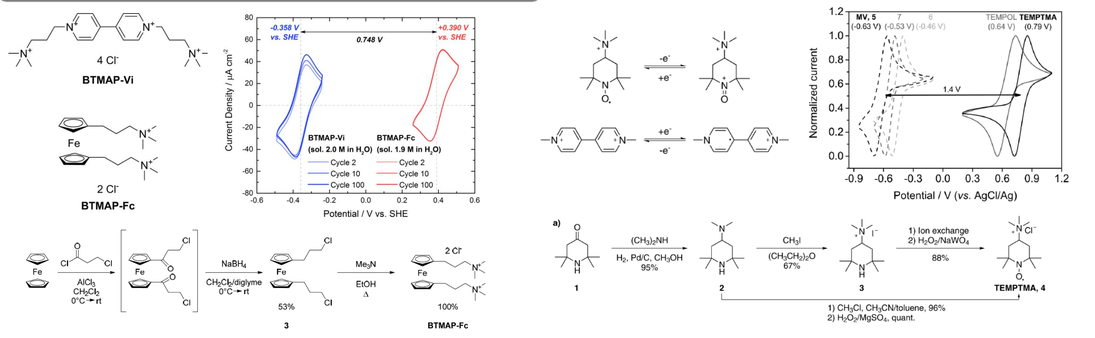
Abstract

Functional group control has been the most widely used strategy to enhance the solubility of redox-active organic material (ROM) in aqueous media. However, these strategies inevitably need organic synthesis which usually requires 2 to 4 steps being cost inefficient and molecule-dependent. In this study, we introduced a surfactant molecule to provide a nonpolar microenvironment via micellisation for higher solubility of ROMs. With cetyltrimethylammonium chloride (CTAC) surfactant, (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO), a representative ROM, showed enhanced solubility of more than 10 times. Despite the electrically insulating nature of micelle, charge transfer of micellar solubilised TEMPO could occur in a quite different mechanism compared with TEMPO in bulk water, resulting in higher energy density. Furthermore, micellar solubilisation induced cycle stability improvement due to not only enhanced chemical stability in oxidised state but also mitigated crossover. This strategy could be applied to various ROMs and expected to be a solution for the practical application of organic flow batteries.

Introduction

Common strategy for high energy density organic flow batteries

Molecular tuning of active material



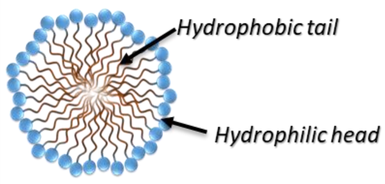
ACS Energy Lett. 2017, **2**, 639−644

Angew. Chem. Int. Ed. 2016, **55**, 1–5

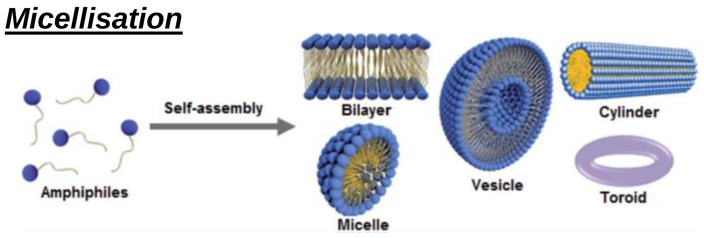
- ✓ Attachment of solubilising group has been most widely used for solubility enhancement of various ROMs.
- ✓ However, this strategy inevitably needs a few organic synthesis steps which require additional economic cost.

Surfactant as a solubilising agent

Composition

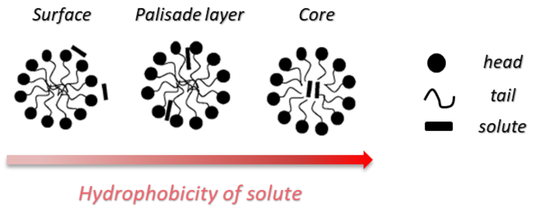


Micellisation



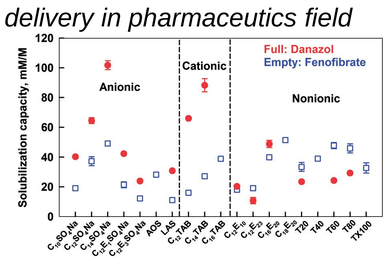
RSC Adv. 2020, **10**, 42098-42115

Micellar solubilisation



J. Pharm. Pharm. Sci. 2005, **8**, 147-163

** Drug delivery in pharmaceutics field*



Drug Dev. Ind. Pharm. 2018, **44**, 677-686

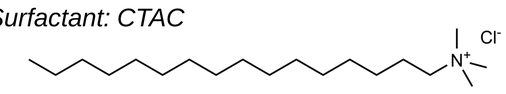
- ✓ Surfactant molecules make self-assembly over critical micelle concentration, providing hydrophobic microenvironment inside the micelle.
- ✓ Organic molecules, mainly composed of hydrophobic hydrocarbon, could be solubilised by micellar solubilisation, resulting in higher solubility and energy density.

Results and Discussion

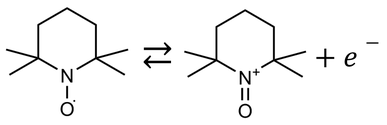
Micellar solubilisation of TEMPO

Material selection

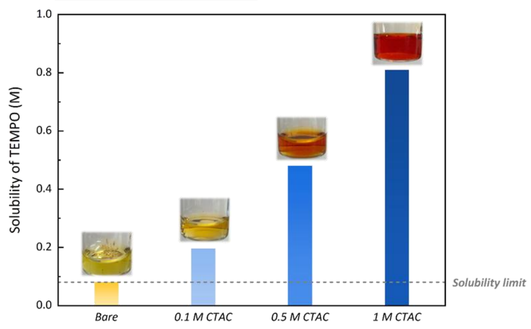
- ✓ *Surfactant: CTAC*



- ✓ *Active material: TEMPO*



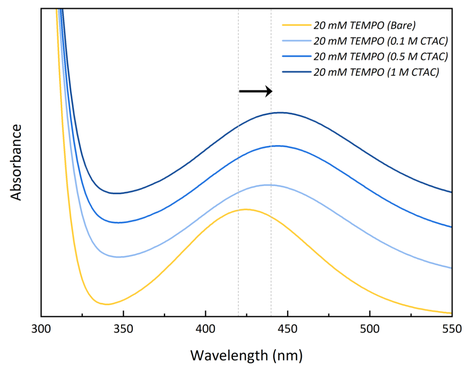
Solubility test



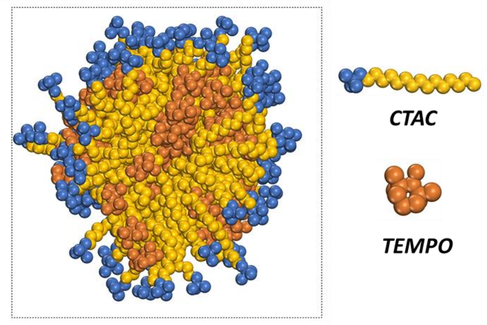
- ✓Solubility of TEMPO was increased by more than 10 times in 1 M CTAC solution.

Evidence of micellar solubilisation

UV-Vis spectra of TEMPO



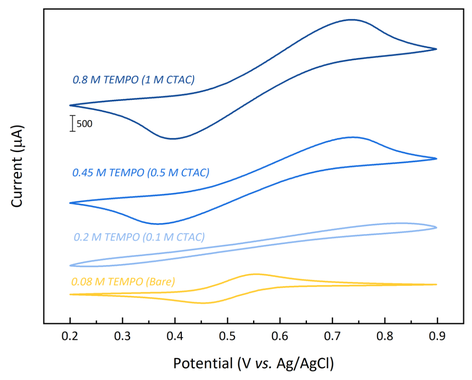
Molecular dynamics (MD) simulation



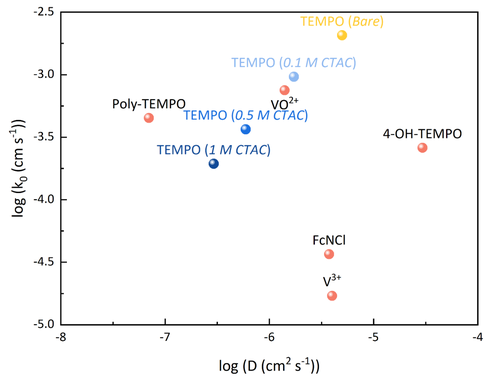
- ✓Red shift of $n\pi^*$ transition absorption peak indicates the change of polarity of local environment, proving the micellar solubilisation of TEMPO.

Electrochemical properties of micellar electrolyte

Cyclic voltammograms



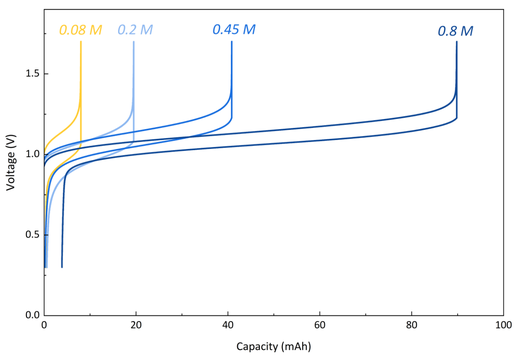
Electrochemical kinetic parameters



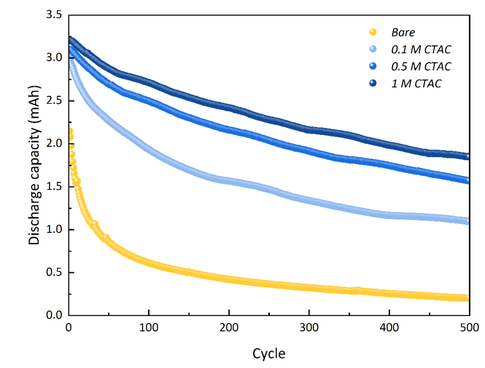
- ✓Redox potential of TEMPO was increased with [CTAC] due to stabilised TEMPO in micelle.
- ✓Kinetic parameters of micellar solubilised TEMPO was decreased but still comparable with various active materials reported before.

Flow cell performance

Electrochemical profile



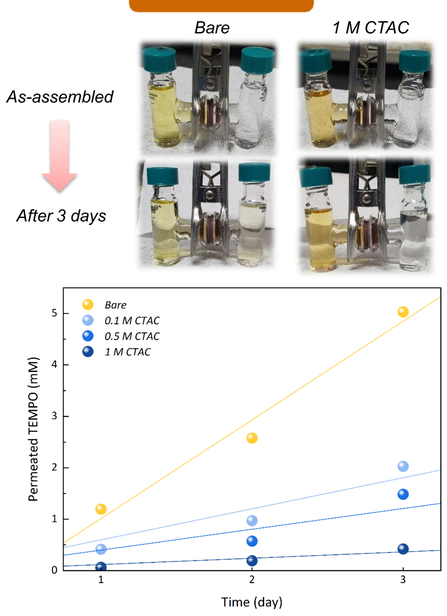
Cycle performance (0.03 M TEMPO)



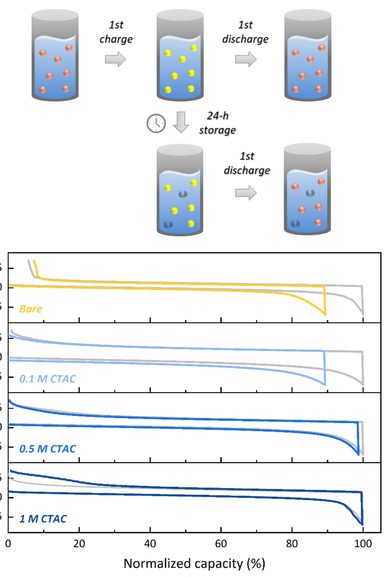
- ✓Increase solubility indeed delivered reversible capacity in the flow cell.
- ✓As a result, energy density was increased more than 10 times.
- ✓Furthermore, capacity retention was improved with [CTAC].

Cycle stability analysis

Crossover



Chemical decomposition



- ✓Crossover of TEMPO was also mitigated with micellar solubilisation due to size effect and low diffusion coefficient.
- ✓Oxidised TEMPO in micelle phase restored higher capacity after 24 hr storage which indicates improved chemical stability in micellar electrolyte.

Conclusion

In this study, organic flow battery with high energy density was achieved by applying a surfactant molecule which can solubilise ROMs via micellisation. We found that TEMPO could be oxidised even in micelle, delivering most of the theoretical capacity. Moreover, micellar solubilisation with surfactant electrolyte induced higher capacity retention compared with that in the conventional electrolyte. This superior performance was originated from not only reduced crossover but also mitigated chemical degradation of oxidised form. Consequently, micellar solubilisation induced higher energy density and long cycle life without any organic synthesis process so that new types of ROMs can be introduced into aqueous system.