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Two electron utilization of methyl viologen anolyte in nonaqueous organic redox flow battery

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ABSTRACT

Methyl viologen (**MV**) as a bench-mark anolyte material has been frequently applied in aqueous organic redox flow batteries (AORFBs) towards large-scale renewable energy storage. However, only the first reduction of **MV** was utilized in aqueous electrolytes because of the insoluble **MV⁰** generated from the second reduction of **MV**. Herein, we report that methyl viologen with bis(trifluoromethane)sulfonamide counter anion, **MVTFSI**, can achieve two reversible reductions in a nonaqueous supporting electrolyte. Paired with (Ferrocenylmethyl)trimethylammonium bis(trifluoromethanesulfonyl)imide, **FcNTFSI**, as catholyte, the **MVTFS/FcNTFSI** nonaqueous organic redox flow battery (NOARFB) can take advantage of either one electron or two electron storage of the methyl viologen moiety and provide theoretical energy density of 24.9 Wh/L and a cell voltage of up to 1.5 V. Using a highly conductive LiTFSI/CH₃CN supporting electrolyte and a porous Daramic separator, the NOARFB displayed excellent cycling performance, including up to a 68.3% energy efficiency at 40 mA/cm², and more than 88% total capacity retention after 100 cycles.

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1. Introduction

Utilization of renewable energy sources such as solar and wind energy represents a sustainable and environmentally benign strategy to alleviate the world's severe dependency on traditional fossil fuels [1]. In order to manage the intermittent and fluctuating nature of solar and wind energy, cost effective technologies for energy conversion and storage are in urgent need [1–3]. Among numerous energy storage technologies, redox flow batteries (RFBs) have been recognized as a promising technology to overcome the intermittency of renewable energy and supply reliable continuing electricity to the electricity grids with a scale up to MW/MWh [2–4]. Generally, a RFB employs redox active materials dissolved in liquid supporting electrolytes. During the charge/discharge process, the anode electrolyte (anolyte) and cathode electrolytes (catholyte) stored in two separated reservoirs are flowed through the electrode chamber [3,4]. Then electrochemical reactions take place on the surface of the electrode to store or release energy. The unique cell design of RFBs empowers a number of attractive technical merits for large-scale energy storage in comparison to traditional static rechargeable batteries. First, RFBs can modulate their energy (the volume of the electrolyte reservoirs) and power (electrode surface

area) independently, which makes the power supplying more facile to manage [2–4]. Second, RFBs can operate at high current and high power densities because of fast electrochemical kinetics and high conductivity of aqueous supporting electrolytes. Third but not last, RFBs represent a safe energy storage technology by using non-flammable aqueous electrolyte materials.

As one of the most studied RFBs, vanadium RFBs have been extensively demonstrated for potential commercialization. In spite of their robust chemistry and high power performance, however, their widely applications suffer from several major drawbacks, [2,3] expensive redox active materials, expensive separators, corrosive electrolytes, and electrolyte crossover. To overcome these technical challenges, we and other groups have developed aqueous organic RFBs (AORFBs) [5–19] and nonaqueous organic RFBs (NAORFBs) [20–33] employing sustainable and abundant redox active organic molecules as a new generation of RFBs for green energy storage. Among explored redox active organic compounds, viologen compounds are especially attractive due to its outstanding stability, redox reversibility, and low costs [13]. Among all numerous reported viologen derivatives, methyl viologen (**MV**) is the simplest and has been used a benchmark viologen anolyte in AORFBs [9,12,13,15]. Our previous studies on **FcNCl/MV** aqueous RFBs have proved its excellent electrochemical stability [9,13,15]. However, only the first reduction of methyl viologen can be utilized in aqueous solutions because of the insoluble **MV⁰** species generated after the second reduction, thus further improvement of cell volt-

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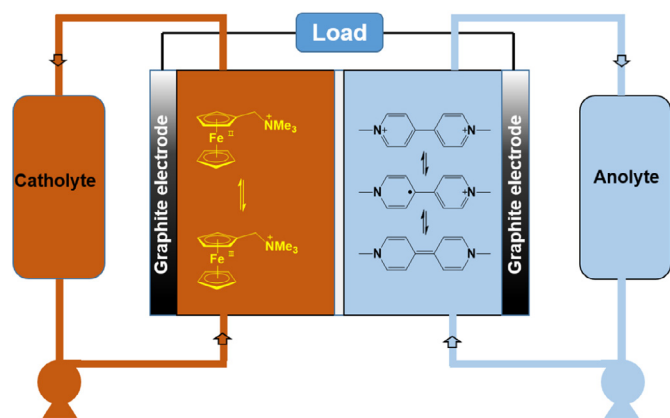


Fig. 1. A schematic representation of the FcNTFSI/MVTFESI NAORFB and cell reactions.

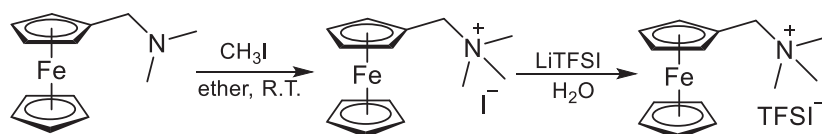
age and capacity, i.e. energy density, was hindered [9,13,15]. In order to utilize the second electron of viologen compounds, we have reported two molecular engineering approaches [16]. In the first molecular engineering approach, we introduced highly hydrophilic pendant ammonium groups into the viologen molecules to ensure the high solubility of the doubly reduced species in aqueous solutions, thereby achieved two electron utilization in AORFBs [16]. In the second molecular engineering approach, we explored a planar thiazolo[5,4-d]thiazole (TTz) framework to extend the conjugation of viologen while functionalizing the pyridinium with hydrophilic ammonium groups to yield a highly water soluble “ π -conjugation extended viologen”, 4,4'-(thiazolo[5,4-d]thiazole-2,5-diyl)bis(1-(3-(trimethylammonio)propyl)pyridin-1-ium) tetrachloride, as a two-electron storage anolyte for AORFB applications [17]. In this study, we report a third approach to realize the direct two electron storage of methyl viologen through a simple anion exchange approach in a NAORFB. Specifically, methyl viologen bis(trifluoromethane)sulfonamide, MVTFESI, was found to display two reversible reductions in a nonaqueous supporting electrolyte. Paired with (Ferrocenylmethyl)trimethylammonium bis(trifluoromethanesulfonyl)imide, FcNTFSI, as catholyte, the MVTFESI/FcNTFSI NAORFB (Fig. 1) can take advantage of either one electron or two electron storage of the methyl viologen moiety and provide a theoretical energy density of 24.9 Wh/L and a cell voltage of up to 1.5V for the two electron utilization of methyl viologen. The demonstrated NAORFBs displayed excellent cycling performance, including up to a 63.3% energy efficiency at 40 mA/cm², and more than 88% total capacity retention after 100 cycles.

2. Experimental

2.1. Chemicals and manipulation

Methyl iodide, 4,4'-bipyridine, and chloroacetic acid were received from Sigma Aldrich. (Ferrocenylmethyl)dimethylamine and Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) were purchased from TCI chemicals. All the chemicals were used as received without further purification.

2.2. Synthesis of (ferrocenylmethyl)trimethylammonium bis(trifluoromethanesulfonyl)imide (FcNTFSI)



(Ferrocenylmethyl)dimethylamine (7.29 g, 30 mmol) was dissolved in 50 mL diethyl ether. To this solution, methyl iodide (5.7 g, 40 mmol) was added dropwise at room temperature. Then the mixture was stirred for 2 hours. The orange precipitate was filtered and washed twice with 20 mL diethyl ether. After the yellow powder was dried under vacuum, it was dissolved in 200 mL deionized water. 10 mL LiTFSI (8.61 g, 30 mmol) aqueous solution was added and stirred for half an hour. The generated orange precipitate was filtered and washed with 200 mL deionized water. After dried under vacuum at 70 °C, the product was collected as an orange powder (15.3 g, 94.8%). ¹H NMR (500 MHz, Acetone-*d*⁶): δ (in p.p.m.), 3.21 (s, 9H), 4.27 (s, 5H), 4.44 (s, 2H), 4.62 (s, 2H), 4.68 (d, 2H). (Fig. S1) Anal. calcd for C₁₆H₂₀N₂O₄F₆S₂: C 36.07, H 3.82, N 5.35; found C 35.61, H 4.05, N 5.26.

2.3. Synthesis of methyl viologen bis(trifluoromethanesulfonyl)imide (MVTFESI)

Methyl viologen dichloride (MVCl₂) was synthesized according to reported procedure [34]. MVCl₂ (10 g, 38.8 mmol) was dissolved in 100 mL deionized water. 10 mL LiTFSI (12 g, 4 mmol) aqueous solution was added and stirred for half an hour. The generated white precipitate was filtered and washed with 200 mL deionized water. After dried under vacuum at 70°C, the product was collected as a white fine powder (28.6 g, 98.9%). ¹H NMR (500 MHz, Acetone-*d*⁶): δ (in p.p.m.) 4.76 (s, 6H), 8.86 (d, 4H), 9.41 (d, 4H). (Fig. S2) Anal. calcd for C₁₆H₁₄N₄O₈F₁₂S₄: C 25.74, H 1.89, N 7.50; found C 25.37, H 1.75, N 7.26.

2.4. Solubility test

Solubility of FcNTFSI and MVTFESI was measured in CH₃CN by preparing a 1.0 mL supersaturated solution in a 5.0 mL graduated cylinder. All the tests were conducted at room temperature.

2.5. Electrochemical studies

2.5.1. Cyclic voltammetry study

All electrochemical CV experiments were carried out in 1.0 M LiTFSI/CH₃CN solutions. Cyclic voltammetry experiments were performed with a Gamry 1000E potentiostat. All potentials were referenced to Fc⁺⁰ by adding ferrocene as internal reference. Glassy carbon working electrode (3 mm diameter) was polished using Al₂O₃ (BAS CF-1050, dried at 150 °C under vacuum) suspended in deionized H₂O, then rinsed with deionized H₂O, and dried with an air flow. Ag/AgNO₃ electrode with 0.1 M AgNO₃/CH₃CN solution inside was applied as reference electrode. A glassy carbon rod (Structure Probe, Inc.) was used as the counter electrode.

2.5.2. Rotating disk electrode study

All linear sweep voltammetry (LSV) studies were conducted using a Gamry 1000E potentiostat in a three-electrode configuration, a glassy carbon disk working electrode (5 mm Teflon-encased glassy carbon disk, Pine Research Instrumentation) along with a glassy carbon counter electrode, and a Ag/AgNO₃ reference electrode as used in CV studies. Before data collection, the electrolyte was purged with Nitrogen gas for 20 min to minimize the O₂ concentration in the solution. The electrode was then rotated from 300 to 2400 rpm with increments of 300 rpm, which was

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