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Substituted Thiadiazoles as Energy-Rich Analytes for Nonaqueous Redox Flow Cells

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ABSTRACT: Understanding structure-property relations is essential for designing energy-rich redox active materials (ROMs) for all-organic redox flow batteries. Herein we examine thiadiazole ROMs for storage of negative charge in the flow cells. These versatile molecules have excellent solubility and low redox potentials, allowing to achieve high energy density. By systematically incorporating groups with varying electron accepting/withdrawing ability, we have examined substituent effects on their properties of interest, including redox potentials, calendar lives of charged ROMs in electrolyte, and the flow cell cycling performance. While the calendar life of energized fluids can be tuned in a predictable fashion over a wide range, the improvements in the calendar life do not automatically translate into the enhanced cycling performance, indicating that in addition to the slow reactions of charges species in the solvent bulk, there are other parasitic reactions that occur only during electrochemical cycling of the cell and can dramatically affect the cycling lifetime.

Redox flow batteries (RFBs) are promising candidates for electrochemical energy storage in the flexible electric grid of the future.¹⁻³ With charged fluids circulating between the storage tanks and power-generating stacks, decoupling of energy storage and power generation can be achieved. Due to this decoupling, customized designs of RFBs can satisfy a wide range of energy/power requirements.⁴⁻⁷ The energy density of a flow cell⁸ is the product of the charge on the carrier, the cell voltage, and the concentration of the carriers. Maximizing this energy density is essential for lowering the costs.⁹⁻¹⁰ Increasing the concentration is the easiest way to achieve this goal without changing cell chemistry,¹¹⁻¹² but another way to the same end is increasing the cell voltage. While zinc based aqueous RFBs could bypass the electrolysis potential of water,¹³⁻¹⁴ the narrow electrochemical window of the typical aqueous solutions limits the latter to < 1.5 V, and surpassing this inherent limitation requires nonaqueous electrolyte.¹⁵⁻¹⁶

Both metal-based complexes and redox active organic molecules (ROMs) have been used for charge storage in such systems.¹⁷⁻¹⁹ ROMs in the positive and negative compartments of a RFB are referred to as catholyte and anolyte molecules, respectively, and the cell voltage is defined by the difference in their redox potentials. Thus, maximization of the voltage requires using ROMs at the extremes of the redox potential range that also need to be stable in solution when charged, which is a difficult requirement to meet. For this reason, the present selection of energy dense ROMs remains limited, while the achieved energy density and cycling stability are still insufficient.²⁰⁻²³ Therefore, designing better ROMs is a high priority.²⁴⁻²⁸

Finding the suitable analytes with the lowest redox potentials proved to be an especially daunting task, as the corresponding radical anions tend to be overly reactive. In this regard, thiadiazoles have been recognized²⁹ as an exceptional class of molecules yielding uncommonly stable radical anions that can be used to store negative charge in RFBs.

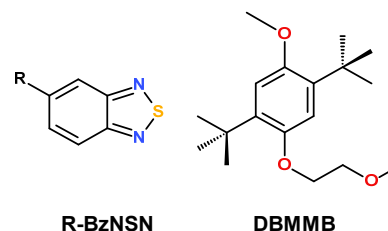


Figure 1. Structural formulase for 2,1,3-benzothiadiazole (R-BzNSN) derivatives and DBMMB. The substituting group R is H (1), CH₃ (2), OCH₃ (3), F (4), and CF₃ (5).

In this report, we examine several thiadiazole ROMs that are based on 2,1,3-benzothiadiazole (BzNSN), **1** (Figure 1), by systematically varying the substituting groups in the arene ring. An anolyte in nonaqueous RFBs needs to meet several property requirements including the low reduction potential, high solubility, low molecular weight, etc. What makes BzNSN unique is that it surpasses almost all other analytes on most of these key properties. (see table S1) The progenitor compound **1** is known to yield stable radical

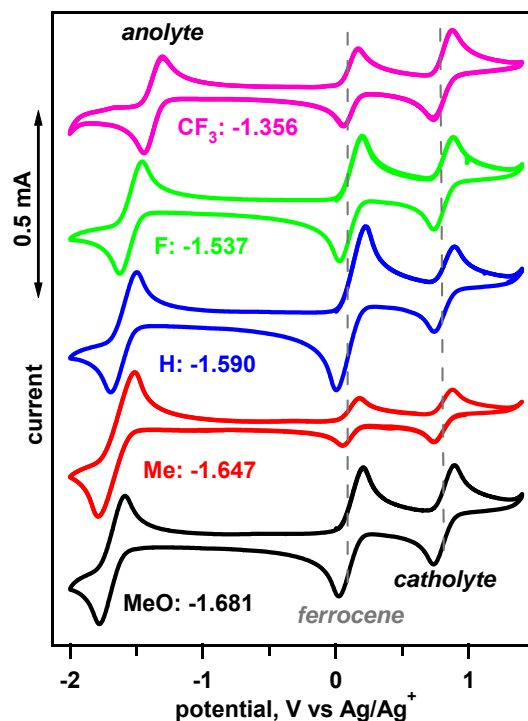


Figure 2. Tuning of the redox potential for BzNSN derivatives (the half-wave potential $E_{1/2}$ vs Ag/Ag^+ is given in the plot) by changing the substituent group R- at carbon-5 of BzNSN. DBMMB catholyte and ferrocene were used as the internal references (both gray dash lines). Cyclic voltammetry of 50 mM ROMs (each) in acetonitrile containing 0.5 M LiTFSI (0.2 V/s). The wave at 0.815 V vs. Ag/Ag^+ corresponds to anodic oxidation of DBMMB. The CV plots have been stacked to facilitate comparison.

anion when chemically or electrochemically reduced. When coupled with 2,5-di-*tert*-butyl-1-methoxy-4-(2'-methoxyethoxy)-benzene (DBMMB in **Figure 1**),^{23, 30} **1** yields cell voltages of ~2.4 V and reasonable cycling at high concentrations (0.1-0.5 M).³⁰

Since BzNSN can be easily derivatized,³¹ a natural question to ask is whether the performance of **1** in the RFBs can be improved further through tuning of the electronic properties of this molecule.

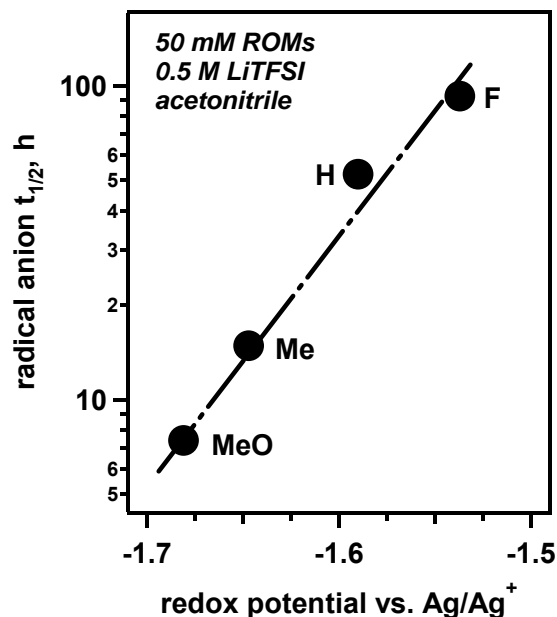


Figure 3. Correlation of the half-decay lifetime $t_{1/2}$ of the radical anions for BzNSN derivatives shown in Figure 1 with the redox potentials $E_{1/2}$ of the parent ROMs given in Figure 2 (50 mM ROMs each, 0.5 M LiTFSI in acetonitrile). Mind the logarithmic vertical scale.

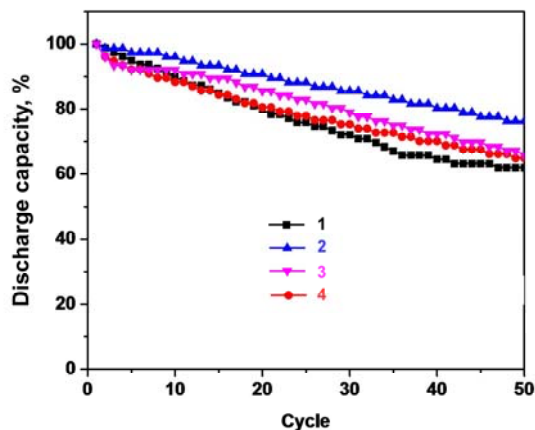


Figure 4. Capacity fade profile (discharge capacity as percentage of the initial capacity) as a function of cycle number for flow cells containing 0.1 M ROMs each in acetonitrile (1.0 M LiTFSI). See the color legend for disambiguation.

To address this question, four functional groups were introduced into **1** at carbon-5 atom as shown in **Figure 1** using the synthetic procedures outlined in section S1 in ESI (see Figures S1 to S7 in ESI for spectroscopic data): a weak (**2**) and a strong (**3**) electron

donating group and a weak (**4**) and a strong (**5**) electron withdrawing group. All of these molecules have excellent solubility in the acetonitrile based electrolytes (> 2 M). The redox behaviors were evaluated using cyclic voltammetry with DBMMB and ferrocene serving as the internal references in acetonitrile containing 0.5 M solution of lithium bis(trifluoromethanesulfonyl) imide (LiTFSI). As shown in **Figure 2**, the half-wave redox potentials $E_{1/2}$ changes as the substituent varies. A density functional theory calculation indicated that the derivatization would change the energetics of the lowest unoccupied molecular orbitals and the reduction potentials in a specific way, as shown in Figure S8 in ESI. In full accord with these theoretical predictions, as the electron withdrawing effect decreases and donating effect increases, the redox potentials decrease from -1.356 V vs. Ag/Ag⁺ for **5** to -1.681 V vs. Ag/Ag⁺ for **3**. The highest value corresponds to the strong electron withdrawing -CF₃ group and the lowest value corresponds to the strong electron donating -OMe group.

To characterize the calendar life stability of charged thiadiazole ROMs in the same electrolyte, these ROMs (50 mM anolyte and 50 mM catholyte) were charged to 100% in an electrochemical H cell (see section S2 and Figure S9 in ESI for more details). Electron paramagnetic resonance (EPR) spectroscopy was used to monitor the decay kinetics for the electrochemically-generated radical anions. The radical anion of **5** was short-lived (< 15 min) possibly due to fluorine loss from the trifluoromethyl group. The half-decay lifetimes $t_{1/2}$ for radical anions of other thiadiazole ROMs are shown in **Figure 3** (under the same experimental conditions, the $t_{1/2}$ for the radical cation of DBMMB was ca. 230 h, see Figure S9(a) in ESI). It is seen from **Figure 3** that there is a linear correlation between the logarithm of the lifetime for an anolyte radical anion and the redox potential of the corresponding parent ROM. Therefore, the calendar lives of charged cell fluids decrease exponentially as the redox potentials of the ROMs become more negative, which indicates that redox potentials of the ROMs and chemical stabilities of their reduced states are two opposing factors that need to be carefully balanced when designing a new molecule. The greatest stability is observed for the radical anion of **4**, whose redox potential is the highest. Since the half-decay lifetimes for these radical anions are less than the half-life of the radical cations of DBMMB in the same solutions (see above), we have expected that cycling performance would be mainly determined by the stability of the reduced anolyte ROMs.

To assess the performance of these ROMs in a realistic setting, flow cell cycling was conducted using mixed anolyte and catholyte ROMs in each compartment with the same supporting electrolyte as in **Figures 2** and **3** (see section S3 in ESI for more details). As seen from **Figure 4**, the derivatization of **1** does lead to improvements over the parent compound. Contrary to the calendar life trends shown in **Figure 3**, all the derivatized BzNSN compounds delivered a better cycling performance compared to **1**. The best performer was compound **2**, which demonstrated 75% capacity retention after 100 cycles. Other derivatives, including the most stable anolyte **4**, delivered only 64-65% capacity retentions, which is only slightly better than 62% of **1**. It is noted that the cycling performance was also evaluated using a static H cell, for which the results were once again different from the trends shown in **Figure 3** but also different from the trends shown in **Figure 4** (see Figures S12). These inconsistent cycling lifetimes suggest that apart from the reactions of charged radical ions in the solvent bulk, there are additional parasitic reactions that affect the performance, which occur only when the cells are continually cycled, and these parasitic reactions strongly depend on the specific cell design and the mode of operation. Understanding the causes for poor correlation between

the calendar and cycling lives of the charged fluids requires more studies to identify and control these unwanted processes.

To conclude, thiadiazole compounds are among the select group of anolyte ROMs that can potentially deliver the sufficient energy density for all-organic RFBs to become competitive with the aqueous flow cells. Our studies suggest that the stability of their radical anions (that is, charged ROMs) in acetonitrile solutions correlates well with the redox potential of the corresponding parent compounds. However, the cycled lives for these anolyte ROMs in the RFB cells did not follow the calendar life trends suggesting the occurrence of additional parasitic reactions, which do not occur during calendar aging of the same charged fluids. Incremental improvement in the cycling performance was obtained for the 2/DBMMB system over our current benchmark 1/DBMMB system.

Thus, combining the high cell voltage (>2.4 V) with the long cycling life (> 1,000 h) in all-organic RFBs remains a challenge, as it is the natural tendency of the radical ions to become exponentially more reactive as the redox potential reach the extremes, as illustrated in **Figure 3**. With these molecules we are on the very edge of possibility, reaching the compromise between the highest energy density and the stability of the radical anion that can be achieved in acetonitrile. This finding strongly indicates the significant role of structural engineering in achieving improvement of radical ion stability, suggesting a generic guidance for developing long-cycling ROM-based flow cells.

ASSOCIATED CONTENT

Supporting Information

Synthesis procedures of derivative molecules, static electrolysis, details of EPR spectroscopy and electrochemical tests.

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Notes

The authors declare no competing financial interests.

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