



Comparing calendar and cycle life stability of redox active organic molecules for nonaqueous redox flow batteries

Jingjing Zhang^{a,b}, Jinhua Huang^{a,b}, Lily A. Robertson^{a,c}, Ilya A. Shkrob^{a,b,*}, Lu Zhang^{a,b}

^a Joint Center for Energy Storage Research, Argonne National Laboratory, Argonne, IL, 60439, USA

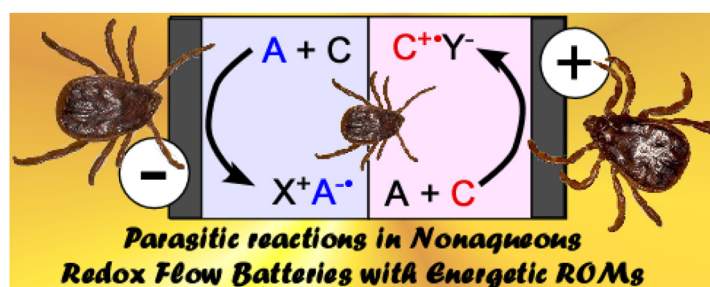
^b Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL, 60439, USA

^c Department of Chemistry, University of Illinois at Urbana-Champaign, 600 S. Mathews Avenue, Urbana, IL, 61801, USA

HIGHLIGHTS

- A family of energetic anolyte molecules has been characterized.
- Chemical stability of charged anolyte molecule has been varied over a wide range.
- Only a weak correlation between the cycle and calendar life stabilities was found.
- This lack of correlation is traced down to the crossover of reaction products.
- Proton leaking membranes are a major roadblock for performance improvements.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Redox active organic molecules
Nonaqueous redox flow batteries
Electrochemical performance
Bulk electrolysis
Cycle life aging
Calendar life aging

ABSTRACT

High stability of energy-rich redox active organic molecules (ROMs) in all states of charge is required for reliable operation of nonaqueous redox flow batteries (NRFBs), in which charged ROMs are used to store electric energy in external reservoirs. Calendar life stability and cycle life stability characterize capacity fade during storage of charged ROMs in the reservoirs vs. continuous cycling of the electrochemical cell. For insufficiently understood reasons, these two metrics of cell performance can be at odds with each other. In this study, we examine ROM systems consisting of dialkoxybenzene and 2,1,3-benzothiadiazole derivatives. By varying ROM structure and electrolyte composition, chemical stability of the charged states is varied over a wide range, and calendar life and cycle life stabilities are compared. For ROM systems that exhibit the highest chemical stability, the cycle life is largely (but not exclusively) limited by parasitic reactions involving the crossover of reaction products between the cell compartments. It appears that in many instances the cycling performance is strongly affected by poor membrane selectivity.

1. Introduction

Redox flow batteries (RFBs) are scalable electric storage devices that compartmentalize charge separation and charge storage [1,2]. In RFBs, large external reservoirs hold energized cell fluids which are charged in electrochemical cells. During the operation, these fluids flow from the

reservoirs through the cell and become charged or discharged [3]. The materials storing positive and negative charges in these fluids are called, respectively, catholyte and anolyte materials. Neutral organic molecules [4–12] and ions [13–15], stable radicals [16,17] transition metal complexes [18,19], organometallic compounds [20], redox active polymers and oligomers [21,22] have all been considered as possible

* Corresponding author. Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL, 60439, USA.
E-mail address: luzhang@anl.gov (I.A. Shkrob).

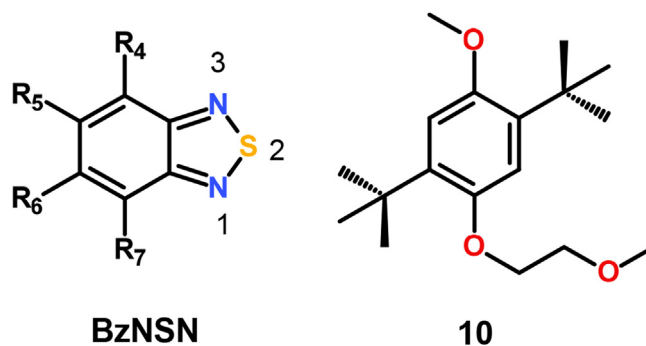
candidates for such RFBs.

As the energy density of storage depends on the cell voltage and the concentration of the charge carriers, organic electrolytes with a wide electrochemical stability window (ESW) theoretically allow a broader range of redox potentials over aqueous electrolytes in which the ESW is narrowed due to water electrolysis [23,24]. Polar organic electrolytes offer other potential advantages that involve improved solubility for many classes of organic molecules and ions and (for carbonate and glyme solvents) compatibility with lithium metal serving as anode in the hybrid flow cells. These advantages, however, need to be weighed against their disadvantages, which include the higher costs and toxicity of organic electrolytes in comparison to aqueous electrolytes, their decreased ability to dissolve electrolyte salts, the reduced heat transfer, etc.

In reality, the potential advantages of the nonaqueous RFBs (NRFBs) have been difficult to implement [25–27] as one needs to combine nearly perfect electrochemistry (that is, minimal interference from parasitic reactions at all stages of RFB operation), high solubility of the redox active materials and high ionic conductivity in all states of charge [28], excellent stability of the charge carriers (that tend to be reactive species), and large difference in their redox potentials (that is the main justification for the nonaqueous RFBs). Despite the conceptual appeal of NRFBs [23], it still remains to be seen that they are a viable and economic path to the grid storage. In particular, the operation life of > 7000 cycles required for this application [29] has not been demonstrated.

Regarding the stability of charged redox active organic molecules, ROMs (e.g., radical ions of the neutral parent molecules), two types of such stability metrics can be distinguished. The stability of separated charges during their storage in the reservoir before the energy is recovered from the fluids can be referred to as the *calendar* life stability; in the ideal case, it is defined by slow chemical reactions of these charged species with other electrolyte components. The ability of the entire RFBs to hold capacity as it is cycled continuously between the charged and discharged states is referred to as the *cycle* life stability. While a ROM system with poor calendar life stability cannot be expected to exhibit good cycle life stability, the opposite is possible as there are numerous additional parasitic reactions that occur only during cell cycling. While the calendar life stability is determined by a relatively few reactions (which make them far more accessible to mechanistic studies), the cycling life reflects complex chemical evolution of the cell as it is cycled. Due to this inherent complexity, the study of such reactions is more descriptive; our goal in this article is to identify the main degradation pathways as opposed to the enumeration and modeling of all possible channels of this degradation, which is impossible at the current state of the art.

The current nonaqueous RFB (NRFB) prototypes typically operate in low concentration ranges (0.05–0.5 M) and cycling regimes that are not practical (fast charge/fast discharge). Even under these conditions, long-term operation proved challenging: the capacity fade is too rapid and cycle life is relatively short (< 10³ h of operation). The problems can be traced to two sources: (i) insufficient control of parasitic reactions and (ii) lack of proper membranes between the cell compartments in such NRFBs. With the exception of macromolecular catholytes and anolytes (e.g., see Refs. [21,22]) in the present day devices, ROMs can cross between the cell compartments during cycling. This crossover can lead to new degradation pathways that deplete active materials and speed up capacity loss. While there is presently abundant literature on ROM development and NRFB performance trials, there is insufficient understanding of the causes for underperformance and failure in such systems, i.e., (i) what specific reactions are responsible for the observed complications? and (ii) are they inherent to ROM chemistry or the consequence of imperfect RFB design? Indeed, even if the cell membrane blocks the cross over of neutral and charged ROMs, these membranes may not be equally selective to the *products* of their decomposition that involve, *inter alia*, the solvated protons that are



Scheme 1. BzNSN Anolyte and Dialkoxybenzene Catholyte ROMs.

particularly difficult to stop. In the absence of ion exchange in the material (and there are currently no ion exchange membranes for organic electrolytes), a membrane that facilitates transport of solvent molecules and supporting ions to carry the current will also carry the proton transport. As energetic radical cations (positive charge carriers) are relatively easy to deprotonate, whereas energetic radical anions (negative charge carriers) are relatively easy to protonate [7,30,31], this unwanted proton transfer could be a major problem for NRFBs. Thus, issues (i) and (ii) are closely related, and the required “perfection” of the cell design may not be practically achievable with the available membrane materials.

Over the last several years, we have been developing ROMs for NRFBs aiming to achieve stable continuous cycling at voltages > 2.4 V [4]. Presently, our best design involves two ROMs: 2,1,3-benzothiadiazole (BzNSN) derivatives (Scheme 1) as an anolyte ROM (A) [4] and an asymmetric dialkoxybenzene [7,32,33] 10 in Scheme 1 as a catholyte ROM, with liquid acetonitrile (CH₃CN) containing 0.5–1 M salts (X⁺Y[−]) serving as the supporting electrolyte. In an ideal RFB device (Fig. 1a) during cell charge, A is reduced to radical anion X⁺A^{−•} on the cathode, while C is oxidized to radical cation C^{•+}Y[−] on the anode. Meanwhile, the salt anions Y[−] and cations X⁺ (along with the electrolyte molecules interacting with these ions) migrate across the membrane between the cell compartments to maintain charge neutrality (while all other species are contained to their respective compartments). This flow of ions is the electric current through the cell. During cell discharge, the radical ions of ROMs are neutralized, and the current flows in the opposite direction. While our flow cell demonstrated continuous high-voltage operation and good cycling stability vs. other state-of-the-art systems, the same general conundrum confronting all RFB developers also confronted us. Was the cycle life of our device controlled by imperfect chemistry, imperfect cell design, or both? Here we present an approach to addressing these concerns.

To this end, we used our cell chemistry as a test bed for analyzing such problems. Our strategy was to chemically modify the anolyte ROM with electron-donating and electron-withdrawing groups to vary the chemical stability of radical anions by varying their redox potentials (see Fig. 2 and Table 1). Spectroscopic and analytical means were used to elucidate factors controlling the stability of X⁺A^{−•} pairs in electrolyte bulk. This part of the study is implemented in Ref. [30] and briefly summarized in section 3.1 to provide the background; here we focus on a different question: how does this calendar life stability relate to the cycle life stability of the redox system? We use *static* cells and operate these cell in low-concentration regimes to bring cycling conditions close to the ideal exemplified in Fig. 1a. In such static cells, relatively thick (0.5–2 mm) ceramic separators can be used instead of thin, permeable membranes in the flow cells. The relatively low ROM concentration (50 mM) in our experiments minimizes (but not fully excludes) the occurrence of electroprecipitation and electroosmosis that are inherent in the high-concentration regimes.

In the course of these studies, it was discovered that even under such “ideal” conditions, the cycle life and calendar life still poorly

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