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The impact of pH on side reactions for aqueous redox flow batteries based on nitroxyl radical compounds

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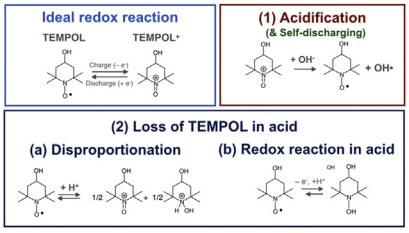
HIGHLIGHTS

- The pH of TEMPOL electrolyte greatly affects the reversibility of its redox reaction.
- Reaction of TEMPOL with OH^- ion causes the decrease of electrolyte pH.
- TEMPOL in an acidic electrolyte leads to a decrease in its concentration.

GRAPHICAL ABSTRACT



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ABSTRACT

Electrochemical and UV-VIS measurements demonstrate that the pH value of a 4-hydroxy-2,2,6,6-tetramethyl-1-pipperidinyloxyl (TEMPOL) electrolyte significantly impacts its redox reversibility. The diffusion coefficient and kinetic rate constant of TEMPOL in neutral aqueous solution are determined and shown to be comparable to those of vanadium ions used for industrially utilized redox flow batteries (RFBs). RFBs that incorporate a TEMPOL catholyte and Zn-based anolyte have an average voltage of 1.46 V and an energy efficiency of 80.4% during the initial cycle, when subject to a constant current of 10 mA cm^{-2}. We demonstrate several factors that significantly influence the concentration and capacity retention of TEMPOL upon cycling; namely, pH and atmospheric gases dissolved in electrolyte. We expand upon the known reactions of TEMPOL in aqueous electrolyte and propose several concepts to improve its electrochemical performance in a RFB. Controlling these factors will be the key to enable the successful implementation of this relatively inexpensive and environmentally friendly battery.

1. Introduction

Redox flow batteries (RFBs) have attracted much attention for use in large-scale energy storage applications, such as in smart grids, because of their many advantages, including their flexible and modular design, as well as fast response time [1–4]. Typical RFBs comprise two electrolyte tanks for storing energy, a cell unit for converting energy, and pumps for circulating each electrolyte (catholyte and anolyte). This unique energy storage system enables the use of many kinds of materials, ranging from inorganic compounds such as vanadium [5], chromium [6], iron [7], bromine [8], and iodine [9,10], to organic compounds like quinone [11] and polysulfide [12]. These RFBs can be subdivided into two types: ones aimed at achieving high-energy density, and others designed for low cost and safety. The former type of batteries, including Li/I [10] and Li/polysulfide [12], are based on high voltages, which result from the low redox potential of Li metal. A myriad of problems involving lithium metal dendrites have yet to be solved, however,

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making the long-term stability of these systems challenging [13]. The latter group of batteries, such as anthraquinone-2,7-disulfonic acid/bromine [11], 2,6-dihydroxyanthraquinone/ferrocyanide [14], and zinc/iodine (Zn/I) [9] are suitable for grid-scale energy storage due to their inherently robust and safe systems. Although some of these aqueous batteries have issues, including the use of toxic bromine, strong alkaline electrolyte, and the formation of Zn dendrites, their cost effective materials and nonflammable electrolytes are definite benefits for grid-scale energy storage.

Recently, an inexpensive cathode material referred to as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) has been explored for use in organic-based electrolytes [15,16]. Its performance when coupled with Li-ion anode is reasonably impressive, with a high energy density of 126 W h L^{-1} [15]. Interestingly, functionalizing the 4-position of TEMPO with a hydroxyl group results in relatively high solubility in water. The functionalized compound, referred to as TEMPOL (4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl), can be dissolved at concentration as high as 3.6 M. In addition, it bears the same sterically protected radical center associated with the delocalized unpaired electron of the N–O bond found in TEMPO [17–19]. For these reasons, TEMPOL may be a promising candidate for use as catholyte in an aqueous redox flow battery of high energy density. Previously, TEMPOL had been studied as catalyst [20], fluorescent probe [21], and electrode modifier in dye-sensitized solar cells [17]. Very recently, its feasibility for use as an electrolyte active material in RFBs has also been explored [22]. The TEMPOL/methylviologen system exhibited slight capacity decay over the course of 100 cycles, especially at high TEMPOL concentrations, but initial performance results were promising. Because the capacity fading mechanism is still unclear, this paper aims to elucidate aspects of the degradation that may arise from aqueous TEMPOL catholyte. The full range of optimized conditions, such as electrolyte pH and supporting electrolyte, have not yet been reported. The existence of side reactions in aqueous TEMPOL electrolyte has also not yet been thoroughly explored.

Nitroxyl radical compounds are known to have complex side reactions in H_2O, besides the ideal and reversible redox reaction observed in TEMPO [23,24]. As shown in Fig. 1, we hypothesize that TEMPOL mirrors the redox reaction of TEMPO both chemically and electrochemically; both the redox and known disproportionation reactions based on TEMPO are shown. Based on these mechanisms we propose that side reactions occur and are influenced by the pH of TEMPOL electrolyte. The effect of pH on the reversibility, diffusion coefficient, and kinetic rate constant of TEMPOL were examined in this study.

We report upon a new aqueous RFB using TEMPOL catholyte and zinc-based anolyte. These aqueous electrolytes can be used without any toxic or corrosive compounds under neutral conditions, and they are also inexpensive. The redox reactions of TEMPOL and the overall reaction of TEMPOL/Zn are shown in (1) and (2).

$$\text{TEMPOL} \rightleftarrows \text{TEMPOL}^{+} + e^{-} \quad E_{1/2} = 0.61 \text{ V vs. Ag/AgCl} \tag{1}$$

$$2\ \text{TEMPOL} + Zn^{2+} \rightleftarrows 2\ \text{TEMPOL}^{+} + \text{Zn} \quad E = 1.59 \text{ V} \tag{2}$$

The effects of both the supporting electrolyte and the separator on battery performance were analyzed. The supporting electrolytes were chosen among NaCl, Na_2SO_4, and $NaClO_4$ – all inexpensive, earth-abundant and relatively safe materials. In addition to Nafion, a hydrocarbon-type anion-exchange membrane (AEM) was tested as a separator. This separator is potentially less expensive than Nafion, a perfluorinated cation-exchange membrane (CEM) that has been commonly used in RFBs because of its high chemical stability [25].

2. Experimental

2.1. Materials

All chemicals, except Nafion, were used as received without any further purification. 4-Hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPOL), sodium sulfate, sulfuric acid, zinc acetate dihydrate, and Nafion 212 were purchased from Sigma-Aldrich. Sodium perchlorate was purchased from EMD Millipore, and sodium

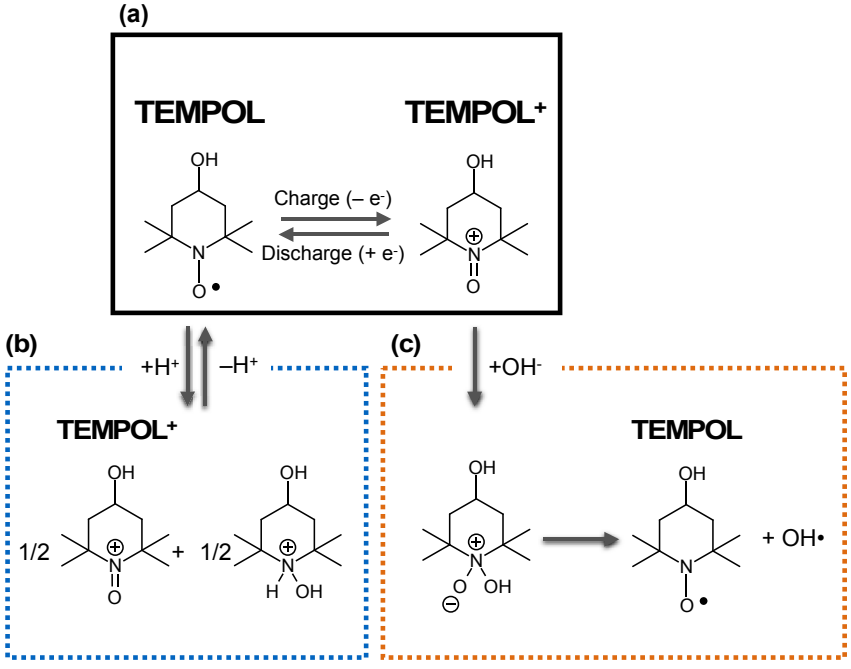

Fig. 1. (a) The ideal redox reaction of TEMPOL, (b) the disproportionation reaction of TEMPOL with H^+, and (c) the chemical reduction of $TEMPOL^+$ with OH^-.