



Stability of molecular radicals in organic non-aqueous redox flow batteries: A mini review

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ABSTRACT

The application of novel organic redox materials is a plausible pathway towards techno-economic energy storage targets due to their low cost and sustainable design. Their operation in non-aqueous redox flow batteries affords researchers the opportunity to innovate, design and optimise these new chemistries towards practical energy densities. Despite this, the identification of high capacity organics which also display long-term stability is inherently challenging due to the high reactivity of molecular radicals.

1. Introduction

Energy management of intermittent renewable resources is a growing challenge for modern grid systems due to a current shortfall of high capacity energy storage implementation. Redox flow batteries (RFBs) are an already established technology which are ideally suited for renewable energy storage due to their decoupled power and capacity [1]. Aqueous designs such as the all-vanadium system [2] (V-RFB) encounter commercial difficulty because RFBs have intrinsically lower energy/power density and higher capital expenditure compared to other battery architectures which operate via electrode intercalation/deposition [3]. A pathway towards higher energy density RFBs is via solvent substitution as the low 1.23 V stability region of water limits the battery cell potential. By operating in a non-aqueous (NA) regime, researchers are afforded a larger design space to develop new materials and plausibly attain high electrolyte energy density via simultaneous enhancement of the cell potential, material solubility and the number of electrons stored per redox species [4]. Energy storage in redox-active organic molecules (ROMs) is a promising new pathway towards low-cost energy storage; however, their application is hindered at present by chemical instability which causes irreversible battery capacity loss. This short review will examine the nascent topic of applying organic neutral and ionic radicals in RFBs and their decomposition reactions in non-aqueous electrolyte. A wealth of literature provides complementary results in which ROMs are evaluated in aqueous media [5–7] and polymer-based designs [8–13].

2. Energy storage in molecular radicals

2.1. Organic redox materials

Early NA RFB literature primarily featured metal coordination complexes (MCCs) such as 2,2'-bipyridine (bpy) [14] or acetylacetonate (acac) [15] compounds. Although materials such as $V(acac)_3$ [16] have realised high theoretical energy densities with cell potentials in excess of 2 V [17], MCCs are relatively insoluble and have low intrinsic capacity – a measure of the number of electrons stored per unit molecular weight. In contrast, low mass ROMs have much higher intrinsic capacity [18] and can be far more soluble in organic solvents (> 1 M) or highly miscible liquids at room temperature [19]. Furthermore, as ROMs may in principle be mass-produced from biomass, they are more likely to achieve economic targets if their energy density is high enough [18]. Despite this, practical application of ROMs is a challenging new field as battery cycling produces chemical species with unpaired valence electrons called radicals which are inherently reactive. As a result, decomposition can rapidly occur via a variety of pathways, often involving the battery solvent or salt [19]. Hence, the chemical conditions of the battery must be carefully considered as the radical shelf-life may be highly dependent on the electrolyte composition, trace oxygen/water, material concentration or temperature. Understanding the reactivity of molecular radicals is therefore key to increasing radical persistence; however, it must first be acknowledged that neutral and ionic radicals are distinctly different chemical species. (See Fig. 1.)

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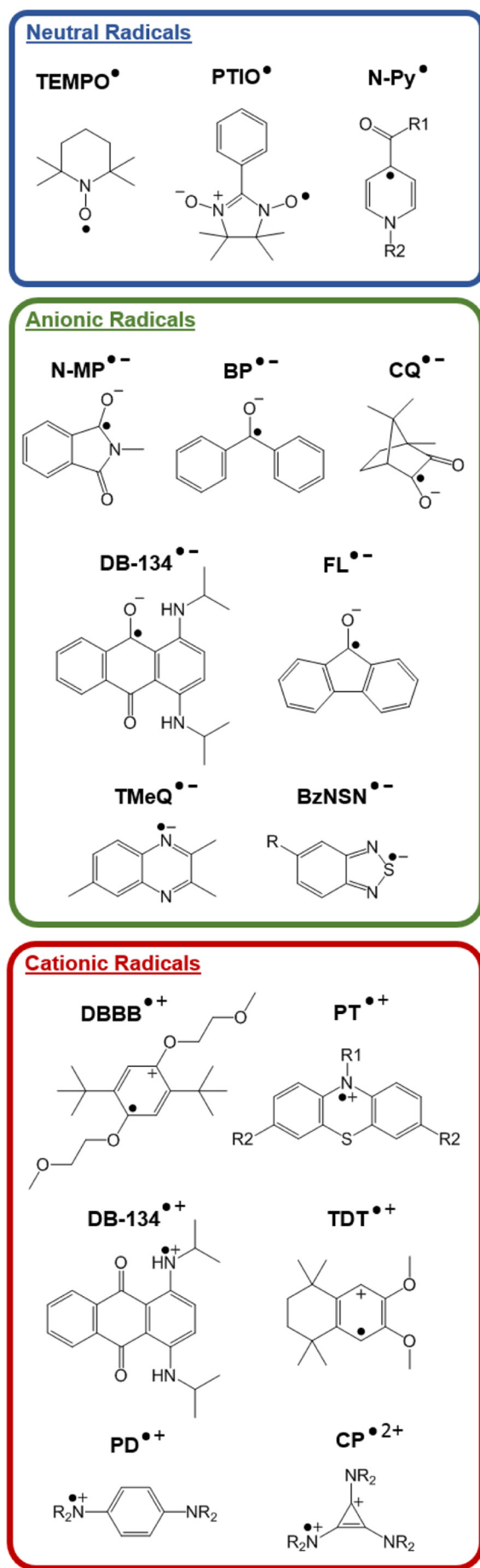


Fig. 1. Chemical structures of redox-active organic molecule radical states described in the text. Readers should note that molecular spin and charge densities can be extensively delocalised and substantially decoupled when the neutral precursor molecule is polar.

2.2. Neutral radicals

Organic molecules are typically uncharged species without any net electron spin because all their valence electrons are paired into discrete molecular orbitals (MOs). Despite this, radicals can be easily generated through bond homolysis to produce species with a singly occupied molecular orbital (SOMO) [20]. Most radicals are reactive because spin-pairing is energetically favoured, hence radical coupling or dimerisation reactions are very facile. In addition, radical reactions with spin-paired molecules, via abstraction or addition mechanisms, are also possible causing the radical to propagate to other molecules and radical chain reactions to occur [21]. Therefore, most radicals are typically short lived as there are a plethora of possible decay pathways, although many stable radicals are known because the unpaired electron can be persistent. Radical stabilisation can be achieved by the presence of electron-withdrawing groups, -donating groups or conjugation near the radical locus; however, steric hindrance can significantly increase shelf-life by physically blocking bond formation [20]. For example, the perchlorotriptyl radical is possibly the most stable organic radical known as it has an estimated half-life of 100 years and is thermally stable to 300 °C in air [21].

The most studied neutral radical for energy storage is the relatively stable 2,2,6,6-tetramethyl-1-piperidinyloxy (**TEMPO[•]**) radical [20,21]. **TEMPO[•]** possesses a nitroxyl radical group which is stable due to steric protection by its methyl substituents preventing dimerisation, and a three-electron bond – a resonance effect involving the nonbonded electron pair on the nitrogen. Originally utilised as a lithium-ion overcharge protection redox-shuttle [22] **TEMPO[•]** derivatives have been applied in hybrid lithium-RFBs [23] and organic NA RFBs [12,24–27], due to their reversible one-electron oxidations to oxoammonium cations [24]. Pairing a **TEMPO[•]** catholyte with lithium results in a ~3.5 V cell potential and high > 180 Wh L⁻¹ theoretical energy density [23,27] because **TEMPO[•]** is soluble over 2 M in carbonate electrolyte [23] or capable of forming a solvated ionic liquid [27]. Such batteries have achieved very high ~99% coulombic (η_C) and 86% energy efficiency (η_E) with nominal capacity fade because of high radical stability. Asymmetric NA RFBs with anolytes *N*-methylphthalimide (**N-MP**) [24], benzophenone (**BP**) [28] and (1*S*)-(+)-camphorquinone (**CQ**) [25] have been explored; however, the system stabilities were not assessed as very limited battery cycling data was reported. A more rigorous stability assessment was achieved for 4-acetamido **TEMPO[•]** in a symmetric single-electrolyte cell which displayed near-constant and -theoretical capacity for 20 cycles [26].

A symmetric all-organic NA RFB was proposed featuring 2-phenyl-4,4,5,5-tetramethylimidazolin-1-oxyl-3-oxide (**PTIO[•]**) as both catholyte and anolyte [29]. **PTIO[•]** is another stable neutral nitroxyl radical; however, in addition to reversible oxidation to an oxoammonium cation, **PTIO[•]** also undergoes reversible reduction to an aminoxy anion giving a 1.73 V cell potential. Validation of the symmetric principle was achieved for **PTIO[•]**, via electron spin resonance (ESR), by proving that the **PTIO⁺** and **PTIO⁻** species do indeed regenerate **PTIO[•]** when mixed, hence allowing a non-selective porous separator to be employed and high 20 mA cm⁻² current density achieved. Despite the high ~2.6 M acetonitrile (MeCN) solubility limit of **PTIO[•]**, only a maximal 0.5 M concentration was demonstrated in a flow cell due to increased electrolyte viscosity and separator crossover. Relatively low 90% η_C and 60% η_E was observed due to self-discharge via electrolyte crossover; however, the cell did not cycle at constant capacity as expected suggesting chemical instability.

The electrochemical reduction of low molecular weight pyridinium

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