

Cyclopropenium Salts as Cyclable, High-Potential Catholytes in Nonaqueous Media

Christo S. Sevov, Sharmila K. Samaroo, and Melanie S. Sanford*

Redox flow batteries (RFBs) represent an emerging technology for grid-scale energy storage to provide the load-leveling necessary for the large-scale integration of renewable energies into the electrical grid.^[1] During RFB operation, solvated anode (anolyte) and cathode (catholyte) compounds flow over current-collecting electrodes. Once charged, these electrolytes are stored in containers separate from the electrodes, thereby decoupling the power rating and storage capacity of the device. Existing RFB electrolytes consist of aqueous solutions of redox-active transition metal salts or organic molecules.^[2] Despite recent advances in aqueous RFBs,^[1c,2f] the energy densities of these systems are ultimately constrained by the small potential window of the aqueous medium (≈ 1.2 – 1.5 V). One strategy to address this limitation would involve transitioning to nonaqueous redox flow batteries (NRFBs), using solvents such as acetonitrile or propylene carbonate that can support cell voltages of up to 5 V.^[3]

While numerous scientific and engineering advances will be required to enable practical NRFBs,^[4] a first essential requirement is the identification of electrolytes that possess both high energy density and high stability under nonaqueous conditions.^[5] High energy density electrolytes must undergo reversible redox reactions at very high (catholyte) or low (anolyte) potentials, and also have high solubility in the battery solvent in all charge states. High stability electrolytes must have long shelf-lives (on the order of weeks) at battery-relevant concentrations in the charged and discharged states and also undergo redox cycling to a high state of charge (SOC) without loss of storage capacity. To date, catholytes possessing the required combination of redox potential, solubility, and stability/cyclability in nonaqueous media have remained elusive.

A variety of small-molecule catholytes have been successfully employed in aqueous RFBs, including derivatives of 2,2,4,4-tetramethylpiperidine *N*-oxide (TEMPO)^[2c–e,h] and quinone.^[2f,6] Several TEMPO,^[7] ferrocene,^[8] and thiazine^[9] derivatives have been successfully translated from aqueous to nonaqueous media, and these generally exhibit high cyclability and shelf-stability in acetonitrile or carbonate solvents. However, these materials undergo redox at relatively low potentials (between 0 and 0.4 V vs Fc/Fc⁺), and thus do not provide cathode potentials higher than those already available in aqueous systems. To overcome the low potentials of these

existing materials, recent efforts have focused on dialkoxyarene derivatives as catholytes for NRFBs.^[10] These molecules undergo redox at higher potentials (0.4 to 0.7 V vs Fc/Fc⁺); however, their shelf-lives and cyclabilities remain modest due to the instability of the charged radical cations in acetonitrile and carbonate solvents. As such, these molecules generally exhibit >20% capacity fade before completing 50 charge–discharge cycles.^[10b,11]

This communication describes the development of a new class of organic catholytes that possess the combination of oxidation at high potential, solubility, shelf-stability, and cyclability needed for NRFB applications. These cyclopropenium (CP) derivatives undergo oxidation at potentials of ≥ 0.8 V versus Fc/Fc⁺ to form radical dications. A systematic study of the impact of substituents on cyclability has enabled the identification of CP molecules that undergo at least 200 charge–discharge cycles at these high potentials with <3% loss of storage capacity. The observed cyclability is consistent with measurements showing that the charged catholytes persist in solution without degradation for greater than one week at 0.25 M concentration and are isolable as pure solids. Finally, one of these molecules is soluble in MeCN to at least 0.7 M in all redox states.

We hypothesized that cyclopropenium derivatives would be attractive catholyte candidates for several reasons. First, these molecules are accessible in a single synthetic step from commercial starting materials.^[12] This straightforward synthesis enables systematic variation of the molecular structure to improve cyclability, redox potential, solubility, and other properties. Second, cyclic voltammetry of some of the earliest reported CP derivatives showed a reversible single electron oxidation at high potential.^[13] Third, CPs have been utilized as ionic solvents, suggesting that they could be highly soluble in NRFB media.^[14] Finally, the cationic charge associated with these materials is expected to lead to enhanced conductivity relative to solutions of neutral redox-active organic molecules.^[15]

We initiated our studies by preparing a small set of tris(di-substituted-amino) CP derivatives that represent a systematic variation to the electronic (1–3) and steric (3–5) properties around the CP ring. As shown in Figure 1a, these molecules were synthesized via the reaction of pentachlorocyclopropane with the corresponding secondary amines. Compounds 1–5 were isolated as analytically pure hexafluorophosphate (PF₆) salts, which are all white solids with solubilities of greater than 1 M in acetonitrile.

We first evaluated 1–5 by cyclic voltammetry (CV) under anhydrous conditions in acetonitrile/LiPF₆. As shown in Figure 1b, all five molecules exhibited chemically reversible redox couples ($i_{pc}/i_{pa} \approx 1$) at potentials of ≥ 0.8 V versus Fc/Fc⁺. The incorporation of electron-withdrawing phenyl groups on the nitrogen atoms resulted in a ≈ 150 mV increase in the

Dr. C. S. Sevov, S. K. Samaroo, Prof. M. S. Sanford
Department of Chemistry
University of Michigan
930 N. University Avenue, Ann Arbor, MI 48109, USA
E-mail: mssanfor@umich.edu



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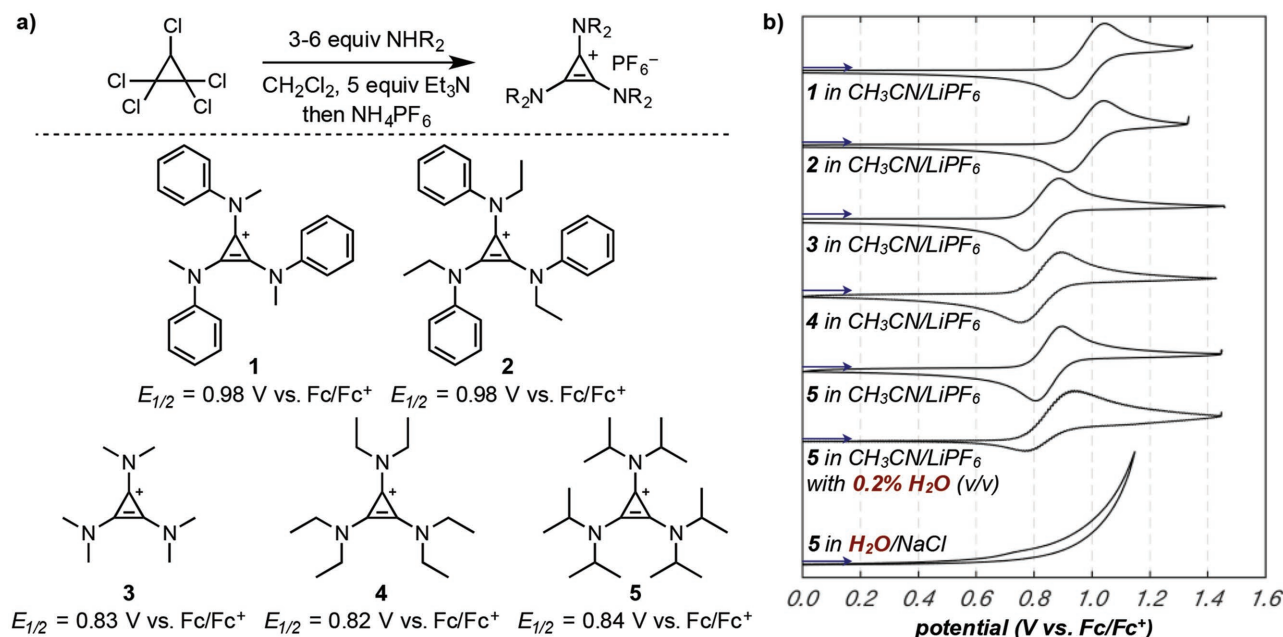


Figure 1. a) Synthesis of CP derivatives 1–5 and their corresponding redox potentials. b) CV of 1–5 as $5 \times 10^{-3} \text{ M}$ solutions under the specified conditions at 100 mV s^{-1} . Blue arrows denote the start and sweep direction.

potential of this redox couple (compare 1 to 3). Notably, the reversibility of the redox couple is highly sensitive to water. For example, CV of a solution of 5 containing just 0.2% water by volume in acetonitrile showed $i_{pc}/i_{pa} = 0.35$, indicating poor chemical reversibility. Furthermore, no redox was observed for a solution of 5 in water/NaCl, likely because the oxidation potential of 5 exceeds the stability window of the aqueous solution. Overall, these results demonstrate that redox reactions of CP salts are well-suited for nonaqueous systems and that these molecules hold promise as high-potential catholytes.

We next performed galvanostatic charge–discharge cycling of $5 \times 10^{-3} \text{ M}$ solutions of compounds 1–5 in acetonitrile/ LiPF_6 using reticulated vitreous carbon (RVC) electrodes. The cycling experiments were conducted as symmetric batteries with the catholyte solution in both compartments of an H-cell that was separated by an ultrafine glass frit. The CPs were charged at a rate of 2.5C with only voltaic cutoffs in order to achieve the maximum SOC possible. Under these conditions, we measured the discharged capacity as a function of cycle for each catholyte to detect any material loss. Furthermore, we monitored the potentials at which cycling occurred to ensure that the measured discharged capacities were at potentials consistent with the redox couples of the CPs, rather than at potentials resulting from decomposed materials.

The results of these cycling studies are plotted in Figure 2a and provide insights into how structural features influence the cycling of the CP molecules. The phenyl-substituted derivatives 1 and 2 exhibited significant decomposition during the first cycle. For these molecules, oxidation initially occurred at the expected potential of 1.0 V versus Fc/Fc^+ (Figure 2b). However, on the second cycle, oxidation took place at a significantly higher potential (1.2 V vs Fc/Fc^+). Importantly, this peak at 1.2 V

is not observed in the CV of the pure material (Figure 1b) and is thus likely due to a redox-active decomposition product formed during the bulk oxidation. Oxidation at this higher potential was the dominant electrochemical reaction in the subsequent cycles (less than 0.8 V vs Fc/Fc^+). The similar cycling profiles of 1 and 2 implicate the phenyl substituent as the source of poor cyclability. We hypothesize that the radical cation in the charged molecules is delocalized into the phenyl π -system. This could then lead to dimerization or nucleophilic attack, analogous to known decomposition pathways of related aryl and anilinium radicals.^[16]

We anticipated that the alkyl CP derivatives 3–5 would be more stable to cycling because the radical dication is not delocalized into high-energy resonance forms. Indeed, the dimethylamino-substituted CP 3 showed dramatically improved cyclability relative to 1 and 2, and underwent 125 charge–discharge cycles at the expected redox potentials prior to 20% capacity fade. The slow fade observed in this system could potentially result from decomposition pathways involving deprotonation of the acidic hydrogens alpha to nitrogen. To impede such pathways, we introduced alkyl substituents to sterically block this potential site of decomposition (compounds 4 and 5). As illustrated in Figure 2a, 4 and 5 can both be cycled 200 times with less than 3% loss of storage capacity. As an example, compound 5 was cycled to an average SOC of 94% and discharged with an average coulombic efficiency of 97%. Charging and discharging occurred at potentials consistent with the measured redox couple of 5 throughout all 200 cycles (Figure 2c). Collectively, these data represent the first examples of stable cycling of

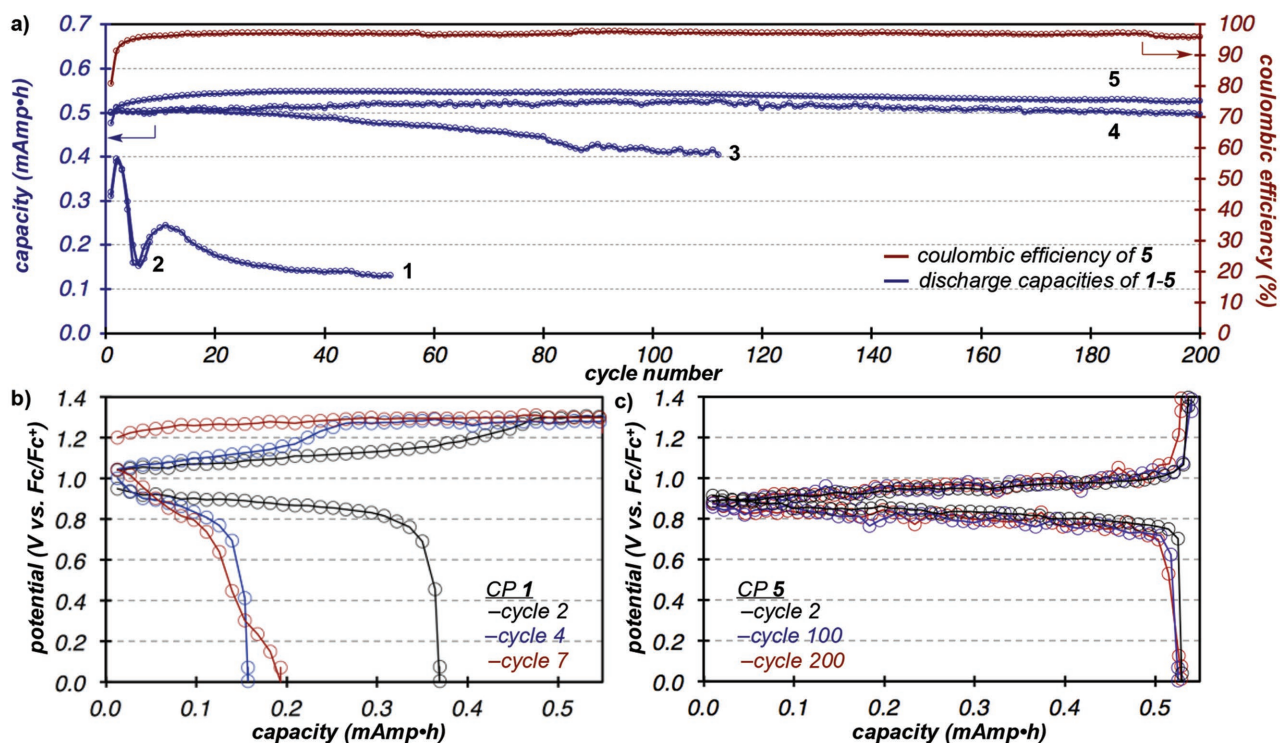


Figure 2. Electrochemical evaluation of CP analogues as catholytes. a) Capacities discharged per cycle for 1–5. b) Selected charge–discharge curves for 1. c) Selected charge–discharge curves for 5.

organic catholytes at potentials that exceed the electrochemical limits of aqueous media.

In addition to stable cycling, a NRFB catholyte must exhibit high shelf-stability in the charged state. To test the shelf-stability of the most cyclable compounds 4 and 5, we electrochemically oxidized 5×10^{-3} M solutions of 4 and 5 in MeCN/LiPF₆ to 4⁺ and 5⁺ (Figure 3a). The resulting red solutions were stored in vials at room temperature in a N₂-atmosphere glove box, and the concentrations of 4⁺ and 5⁺ were monitored over time by CV. Under these conditions, both 4⁺ and 5⁺ exhibit no detectable degradation over one week. We also monitored a 250×10^{-3} M solution of 4⁺ over the same time period (Figure 3b). Even at this high concentration, no degradation of 4⁺ was detected after one week at room temperature.

To gain insights into possible degradation pathways, we subjected separate solutions of 5⁺ to dry air and to degassed water. After exposing the red solution to dry air for 2 h, no color change was detected. CV of this solution showed the expected redox couple for compound 5⁺ with no sign of decomposition products. In contrast, the addition of 2% water to an acetonitrile-*d*₃ solution of 5⁺ resulted in bleaching of the deep red color after 15 min. Analysis of the resulting colorless solution by ¹H and ¹³C NMR spectroscopy revealed diamagnetic resonances that are consistent with the regeneration of 5. These results indicate that the radical dication 5⁺ is compatible with oxygen and that water does not irreversibly degrade 5⁺, but rather serves as a reductant to form 5.

The electrochemically generated radical dications 4⁺ and 5⁺ could be isolated as analytically pure solids by recrystallization

from a mixture of acetonitrile–diethyl ether at –30 °C. These compounds were characterized by CV, elemental analysis, and electron paramagnetic resonance (EPR) spectroscopy. The EPR spectra of frozen acetonitrile solutions of 4⁺ and 5⁺ at 130 K show resonances with *g*-factors of 1.997, consistent with organic radicals.^[17] Single crystals of 5⁺ suitable for X-ray diffraction were obtained by recrystallization from acetonitrile at –30 °C. As shown in Figure 3c, the solid-state structure reveals that all three nitrogen atoms are sp²-hybridized and in the plane of the ring, indicating that the radical cation is delocalized between all three amine substituents. As a result of this geometry, the protons alpha to nitrogen are sterically inaccessible for deprotonation and subsequent catholyte degradation. This likely accounts for the improved stability and cyclability of 4⁺ and 5⁺ relative to the other derivatives.

Finally, we investigated the solubility of the isolated radical dications 4⁺ and 5⁺ in acetonitrile. Compound 4⁺ was found to be soluble up to 0.73 M, which is similar to the 1.7 M solubility of 4. In marked contrast, the solubility of 5⁺ was just 0.081 M in acetonitrile, nearly an order of magnitude lower than that of 4⁺ (0.73 M) and 20-fold less than that of 5 (1.5 M). This result shows that seemingly minor structural changes (replacing ethyl with isopropyl groups) can have a dramatic impact on the solubility of the CP salts (and thus their utility as catholytes).

In summary, this report describes the evaluation of five cyclopropenium derivatives for applications as catholytes in NRFBs. A CP derivative was identified that possesses the rare combination of a high-potential redox couple, high solubility in acetonitrile, and high stability in all redox states. The charged

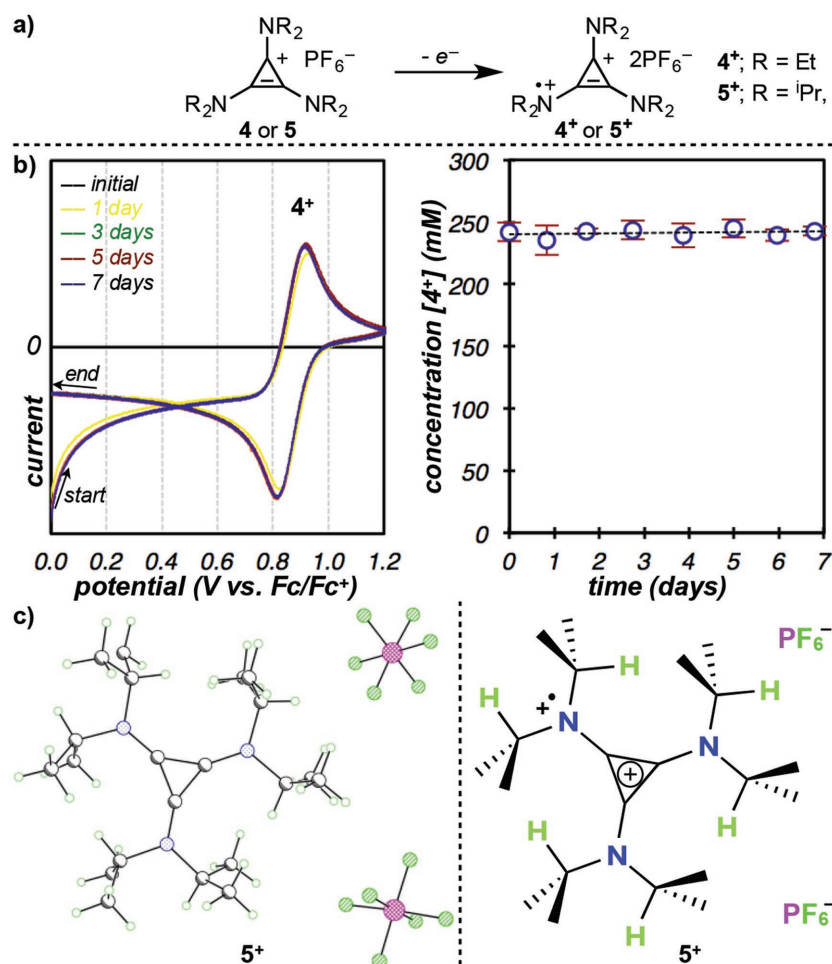


Figure 3. a) Electrochemical generation of 4⁺ and 5⁺. b) Overlaid CVs of diluted aliquots from a 0.25 M solution of 4⁺ over one week (left) and measured concentrations of 4⁺ (right). c) PLUTO and Chemdraw representations of the solid-state structure of 5⁺.

catholytes can be stored for greater than one week without degradation and can be isolated and characterized by X-ray diffraction. Furthermore, these catholytes undergo charge–discharge cycling to nearly 100% SOC for at least 200 cycles with <3% decomposition. Overall, compound 4 has the most promising combination of solubility at all redox states, stability at high concentrations, and cyclability for application as a catholyte in a NRFB. Ongoing work is focused on identifying second generation CP analogues in combination suitable membranes to limit crossover and thus enable evaluation of these catholytes in a full NRFB.

Experimental Section

Materials: Pentachlorocyclopropane^[18] and compounds 3,^[14] 4,^[14] 5^[19] were prepared according to literature procedures. Battery-grade LiPF₆ was purchased from Oakwood Chemical, dried under vacuum at 120 °C for 48 h, and stored in an N₂-atmosphere drybox. Anhydrous acetonitrile (99.8%) was purchased from Sigma-Aldrich and used as received.

Synthesis of 5⁺: In a nitrogen-filled glovebox, a 5.0 mL volumetric flask was charged with 5 (121 mg, 0.250 mmol) and TBAPF₆

(TBA = tetrabutylammonium) (0.970 mg, 2.50 mmol). Anhydrous acetonitrile was added to dissolve the solids and bring the total volume to 5.0 mL. The resulting clear, colorless solution was charged into the side with the working electrode of the H-cell (4.5 mL) via syringe, and the counter side of the H-cell was charged with a solution of 0.50 M TBAPF₆ in acetonitrile. Electrolysis was performed under the standard electrochemical conditions with a current of 10 mA (see charge–discharge cycling below). Once the voltaic cutoff of 1.5 V was reached, the resulting red solution was transferred to a 20 mL screw-capped vial, sealed, and placed in the freezer (−30 °C). After 24 h, a red precipitate had formed. The residual solution was decanted, and the red solids were rinsed with a 1:1 solution of diethyl ether:acetonitrile (5 mL) followed by pure diethyl ether (5 mL). Residual solvent impurities were removed under vacuum to yield 5⁺ as a red solid (125 mg, 89% yield). EPR (acetonitrile, 130 K) 333.8 mT, *g*-factor = 1.997; Anal. calcd. for C₂₁H₄₃F₁₂N₃P₂: C 40.19, H 6.91, N 6.70; found: C 40.10, H 6.62, N 6.60.

Synthesis of 4⁺: Compound 4⁺ was prepared in analogy to compound 5⁺ but utilizing 4 (149 mg, 0.375 mmol). Compound 4⁺ was isolated as a red solid (94 mg, 46% yield). EPR (acetonitrile, 133 K) 333.8 mT, *g*-factor = 1.997; Anal. calcd. for C₁₅H₃₀F₁₂N₃P₂: C 33.22, H 5.58, N 7.75; found: C 33.29, H 5.68, N 7.64.

Charge–Discharge Cycling: Cycling studies were performed on 5.0 × 10^{−3} M solutions of the CP derivatives with 0.50 M LiPF₆ in anhydrous acetonitrile. Using an H-cell with an ultrafine glass frit as the separator, charging and discharging was performed as a symmetric battery with the CP salt in both compartments at a RVC electrode (100 ppi) under galvanostatic control (4 mA, 36 cm² active surface area). During the charge cycles, voltaic cutoffs were set to 1.4 V and the discharge cutoff was set to 0 V. RVC was used as the counter electrode.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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