Video Article A Protocol for Electrochemical Evaluations and State of Charge Diagnostics of a Symmetric Organic Redox Flow Battery

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Abstract

Redox flow batteries have been considered as one of the most promising stationary energy storage solutions for improving the reliability of the power grid and deployment of renewable energy technologies. Among the many flow battery chemistries, non-aqueous flow batteries have the potential to achieve high energy density because of the broad voltage windows of non-aqueous electrolytes. However, significant technical hurdles exist currently limiting non-aqueous flow batteries to demonstrate their full potential, such as low redox concentrations, low operating currents, under-explored battery status monitoring, *etc.* In an attempt to address these limitations, we recently reported a non-aqueous flow battery based on a highly soluble, redox-active organic nitronyl nitroxide radical compound, 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (PTIO). This redox material exhibits an ambipolar electrochemical property, and therefore can serve as both anolyte and catholyte redox materials to form a symmetric flow battery chemistry. Moreover, we demonstrated that Fourier transform infrared (FTIR) spectroscopy could measure the PTIO concentrations during the PTIO flow battery. With a detailed description, we experimentally demonstrated the route to achieve such purposes. This protocol aims to spark more interests and insights on the safety and reliability in the field of non-aqueous redox flow batteries.

Video Link

The video component of this article can be found at https://www.jove.com/video/55171/

Introduction

Redox flow batteries store energy in liquid electrolytes that are contained in external reservoirs and are pumped to internal electrodes to complete electrochemical reactions. The stored energy and power can thus be decoupled leading to excellent design flexibility, scalability, and modularity. These advantages make flow batteries well-suited for stationary energy storage applications for integrating clean yet intermittent renewable energies, increasing grid asset utilization and efficiency, and improving energy resiliency and security.^{1,2,3} Traditional aqueous flow batteries suffer from limited energy density, mostly due to the narrow voltage window to avoid water electrolysis.^{4,5,6,7,8} In contrast, non-aqueous electrolytes based flow batteries are being widely pursued because of the potential for achieving high cell voltage and high energy density.^{9,10} In these efforts, a variety of flow battery chemistries have been investigated, including metal-coordination complexes, ^{11,12} all-organic, ^{13,14} redox active polymers, ¹⁵ and lithium hybrid flow systems.^{16,17,18,19}

However, the potential of non-aqueous flow batteries has yet to be fully demonstrated due to the major technical bottleneck of limited demonstration under flow battery-relevant conditions. This bottleneck is closely associated with a number of performance-limiting factors. First, the small solubility of most electroactive materials leads to low energy density delivery by non-aqueous flow cells. Second, the rate capability of non-aqueous flow batteries is largely limited by the high electrolyte viscosity and resistivity at relevant redox concentrations. The third factor is the lack of high-performance membranes. Nafion and ceramic membranes show low ionic conductivity with non-aqueous electrolytes. Porous separators have demonstrated decent flow cell performance, but suffer considerable self-discharge because of relatively large pore size.^{14,20} Typically, mixed-reactant electrolytes containing both anolyte and catholyte redox materials (1:1 ratio) are used to reduce redox materials crossover, which however sacrifices the effective redox concentrations, typically by half.^{14,21} Overcoming the aforementioned bottleneck requires improvements in materials discovery, battery chemistry design, and flow cell architecture to achieve battery-relevant cycling.

Battery status monitoring is essentially important for reliable operations. Off-normal conditions including overcharge, gas evolution, and material degradation can cause damages to battery performance and even battery failure. Especially for large-scale flow batteries involving large

amounts of battery materials, these factors can cause serious safety issues and investment loss. State of charge (SOC) describing the depth of charge or discharge of flow batteries is one of the most important battery status parameters. Timely SOC monitoring can detect potential risks before they reach threatening levels. However, this area seems to be under-addressed so far, especially in non-aqueous flow batteries. Spectrophotoscopic methods such as ultraviolet-visible (UV-vis) spectroscopy and electrolyte conductivity measurements have been evaluated in aqueous flow battery for SOC determination.^{22,23,24}

We have recently introduced a novel symmetric non-aqueous flow battery design based on a new ambipolar redox material, 2-phenyl-4,4,5,5tetramethylimidazoline-1-oxyl-3-oxide (PTIO).²⁵ This flow battery holds the promise to address the aforementioned challenges of non-aqueous flow batteries. First, PTIO has a high solubility (2.6 M) in the battery solvent of acetonitrile (MeCN) that is promising to enable a high energy density. Second, PTIO exhibits two reversible redox pairs that are moderately separated and thus can form a symmetric battery chemistry by itself. We have also demonstrated that a distinguishable PTIO peak in the FTIR spectra can be correlated with the concentration of unreacted PTIO in the flow cell, which leads to spectroscopic determination of the SOC, as cross-validated by ESR results.²⁶ Here we present a protocol to elaborate procedures for electrochemical evaluations and FTIR-based SOC diagnostics of the PTIO symmetric flow battery. This work is expected to trigger more insights in maintaining the safety and reliability during long-term flow battery operations, especially in real-world grid applications.

Protocol

Note: All the solution preparations, cyclic voltammetry (CV) tests, and flow cell assembly and tests were carried out in an argon-filled glove box with water and O_2 levels less than 1 ppm.

1. Electrochemical Evaluations of PTIO Flow Cells

1. CV Test

- 1. Polish a glassy carbon electrode with 0.05 μm gamma alumina powder, flush it with deionized water, put it in under vacuum at room temperature for overnight, and transfer it into a glove box.
- Dissolve silver nitrate (8.5 mg) with MeCN (5 mL) in the glove box, *i.e.*, 10 mM AgNO₃. Add the solution into the glass tube of a silver/ silver nitrate reference electrode.
- 3. Assemble the glassy carbon working electrode, a graphite felt strip counter electrode, and the silver/silver nitrate reference electrode on a 25 mL three-neck pear-shaped flask.
- Dissolve PTIO (52 mg) and tetrabutylammonium hexafluorophosphate (TBAPF₆, 0.87 g) in MeCN (1.10 g), *i.e.*, 0.1 M PTIO/1.0 M TBAPF₆. Add the solution to the flask to submerge the tips of the three electrodes.
- 5. Connect the electrodes to an electrochemical workstation. Measure the CV curves within the voltage range of -1.75-0.75 V at a scan rate of 100 mV/s. Determine the theoretical cell voltage of the PTIO flow battery by the potential gap between the two redox pairs. NOTE: It should be noted that the Ag/Ag⁺ reference electrode configuration is a pseudo-reference electrode by its nature. As a result, redox peaks might shift during long-term CV measurements. Nevertheless, such shift normally has a negligent influence on the voltage gap between redox couples, and would not affect the cell voltage value.

2. Flow Cell Assembly

- 1. Cut the graphite felts to an area of 1 x 10 cm² using a razor blade. Similarly, cut a porous separator to an area of 3 x 12 cm².
- 2. Dry the flow battery parts (cell compartments, tubing, 5 mL glass vials, graphite felts, and a porous separator) in a vacuum oven at 70 °C for overnight, move them into the glove box, and cool down to the environmental temperature.
- 3. Assemble the flow cell parts in the order of an end plate, a copper plate current collector, a half cell, a graphite felt, a gasket, a porous separator, a graphite felt, a half cell, a copper plate current collector, and an end plate. Fasten the assembly with eight threaded bolts against the two end plates using a torque wrench pre-set at 125 inch pounds. Connect the electrolyte flow tubings to the flow cell. The cell assembly is shown in **Figure 1**.

3. Demonstration of Symmetric Electrochemistry

- Assemble the flow cell according to Section 1.2. Dissolve PTIO (10 mg) and TBAPF₆ (3.3 g) with MeCN (4.4 g) in the glove box, *i.e.*, 5.0 mM PTIO/1.0 M TBAPF₆. Add 4 mL of the solution to each of the two glass vials. Pump the electrolytes to flow using a peristaltic pump at a flow rate of 20 mL/min.
- 2. Connect the positive and negative current collectors of the flow cell to the battery tester. Charge the flow cell at a constant current density of 5 mA/cm² until the voltage reached 1.9 V. Stop the charging. Pump out the electrolytes into the glass vials.
- 3. Mix a 1 mL positive electrolyte with a 1 mL negative electrolyte in a separate vial. Now there are four electrolytes: the original, the positive, the negative, and the mixed.
- 4. Measure electron spin resonance (ESR) spectrum of the above four electrolytes.²⁵
 - With tube sealant, seal a small amount (~10 μL) of the positive and negative in a PTFE tubing (1/16" OD and 1/32" ID) at both ends, and then seal it in a quartz ESR tube (4 mm diameter).
 - 2. Mount the ESR tubing to an ESR spectrometer fitted with an SHQE resonator with microwave frequency ~9.85 GHz (X band).
 - 3. Collect the ESR spectrum for the four electrolytes in Section 1.3.3.

4. Flow Cell Test

- 1. Assemble a flow cell following Section 1.2.
- Dissolve PTIO (1.05 g) and TBAPF₆ (3.50 g) with MeCN (3.60 g) in the glove box, *i.e.*, 0.5 M PTIO/1.0 M TBAPF₆. Add 4 mL of the solution to each glass vial. Flow the electrolytes at 20 mL/min.
- 3. Connect the positive and negative current collectors of the flow cell to an electrochemical workstation. Measure the impedance of the flow cell in the frequency range from 100 kHz to 1 Hz at the open circuit potential. Calculate the area-specific resistivity (ASR) by multiplying the ohmic resistance (high-frequency impedance) by the active area of the flow cell.

4. Connect the positive and negative current collectors of the flow cell to the battery tester. Set up the voltage cutoffs of 0.8 and 2.2 V and the constant current of 20 mA cm⁻² in the battery operation software. Repeatedly charge/discharge the PTIO flow cell.

2. FTIR-based SOC Determination

1. FTIR Feasibility Validation

- Prepare the following three electrolyte solutions in the glove box: (a) MeCN (0.50 g); (b) TBAPF₆ (0.23 g) with MeCN (0.30 g), *i.e.*, 1.0 M TBAPF₆; (c) PTIO (75 mg) and TBAPF₆ (0.25 g) with MeCN (0.26 g), *i.e.*, 0.5 M PTIO/1.0 M TBAPF₆.
- 2. Measure FTIR for the three electrolyte solutions.
 - 1. Add a small volume (~0.05 mL) of each solution to a sealable FTIR cell with KBr windows and a path length of 0.2 mm. Seal the FTIR cell.
 - 2. Put the FTIR cell into a storage container and transfer it out of the glove box.
 - 3. Quickly mount the FTIR cell to a spectrometer and collect the FTIR spectrum.
- 3. Assemble a flow cell following Section 1.2.
- Dissolve PTIO (1.05 g) and TBAPF₆ (3.50 g) with MeCN (3.60 g) in the glove box, *i.e.*, 0.5 M PTIO/1.0 M TBAPF₆. Add 4 mL of the solution to each glass vial. Flow the electrolytes at 20 mL/min.
- 5. Fully charge the flow cell until the voltage reaches 2.2 V. Stop the charging and the pump.
- 6. Measure the FTIR spectra for both the positive and negative electrolytes, respectively, following the procedure in Section 2.1.2.
- 7. Prepare a series of PTIO solutions (0.05-0.5 M) in 1.0 M TBAPF₆ in MeCN in the glove box with the compositions in **Table 1**.
- 8. Measure the FTIR spectrum for each of the solutions in Section 2.1.6, following the procedure in Section 2.1.2.

2. FTIR Measurement of SOC

- 1. Assemble a flow cell following Section 1.2.
- Dissolve PTIO (2.9 g) and TBAPF₆ (9.6 g) with MeCN (9.8 g) in the glove box, *i.e.*, 0.5 M PTIO/1.0 M TBAPF₆. Add 11 mL of the solution to each of the two glass vials. Flow the electrolytes at 20 mL/min.
- 3. Charge the flow cell at a constant current of 10 mA/cm² at a flow rate of 20 mL/min.
- 4. At the charge time of 0, 18, 36, 54, and 72 min, stop the cell charge and electrolyte flow, take small aliquots (0.2 mL) of the electrolytes from anolyte and catholyte side glass vials, and then resume the cell.
- 5. Measure the FTIR spectrum for the above five sample aliquots, following the procedure in Section 2.1.2.
- 6. Measure the ESR spectrum for the above five sample aliquots, following the procedure in Section 1.3.4.

Representative Results

The unique advantages of the symmetric PTIO flow battery system are highly ascribed to the electrochemical properties of PTIO, an organic nitroxide radical compound. PTIO can undergo electrochemical disproportionation reactions to form $PTIO^+$ and $PTIO^-$ (**Figure 2a**). These two redox pairs are moderately separated by a voltage gap of ~1.7 V (**Figure 2b**) and can be used as both anolyte and catholyte redox materials in a symmetric battery chemistry. Using PTIO as a redox material can eliminate the need for mix-reactant electrolytes and enable high effective redox concentrations.

The reaction between PTIO⁺ and PTIO⁻ spontaneously regenerates the original PTIO, as demonstrated by the recovery of the ESR signal of PTIO after mixing PTIO⁺ and PTIO⁻ at equal molar concentrations (**Figure 2c**). In this flow battery, the crossover of charged PTIO species (PTIO⁺ or PTIO⁻) does not result in disparate chemicals and material loss, leading to minimal irreversible crossover. The PTIO flow cell delivered decent cycling efficiencies at a redox concentration of 0.5 M PTIO and with a current of 20 mA/cm; an average coulombic efficiency (CE) of ~90%, voltage efficiency (VE) of 67%, and energy efficiency (EE) of 60% were obtained (**Figure 2d**). The low VE was registered by the relatively high cell ASR of 21.2 Ω cm² that was closely associated with limited ionic conductivity at such a high electrolyte concentration. Despite the capacity fading, the PTIO flow cell has demonstrated operating redox material concentration, current density, and cell efficiency significantly higher than many other non-aqueous RFBs, which cycled typically near 0.1 M concentrations, with current densities less than 0.5 mA/cm², and/ or EEs no higher than 50%.^{27,28,29,30}

FTIR has successfully validated its qualifications as a suitable SOC-diagnosing tool for the PTIO flow battery, because of the characteristic FTIR peak at 1,218 cm⁻¹ that presumably corresponds to the N-O bond.³¹ First, the supporting MeCN solvent and TBAPF₆ salt produce negligible interference peaks at this position (**Figure 3a**). Second, FTIR distinguishes among the three redox species of PTIO, especially with disappearance of this peak for PTIO⁺ at the catholyte side (**Figure 3b**). Third, the intensity (T) of this peak displays a strong dependence on the PTIO concentration (**Figure 3c** and inset), *i.e.*, a linear -log(T) vs. [PTIO] standard relationship (Equation 1) is obtained according to the Beer-Lambert Law:

$-\log(T) = 1.11[PTIO] + 0.156$ (1)

The five sample aliquots taken from the catholyte side (**Figure 4a**) were used to determine the SOC of the PTIO flow cell. As the charging time proceeded from Sample #0 to #4, the intensity of the 1,218 cm⁻¹ peak continuously decreased due to consumption of PTIO (**Figure 4b**); so was the ESR signal (**Figure 4c**). The concentrations of unreacted PTIO in these samples were derived by the FTIR intensities of the 1,218 cm⁻¹ peak according to Equation 2, which then was used to calculate the SOC following Equation 2. As shown in **Figure 4d**, such obtained [PTIO] and SOC of these samples are in close agreement with the ESR measurements, which appears to be a good cross-validation.

$$SOC = \frac{[PTIO^+]}{[PTIO^+] + [PTIO]} \times 100\% = \frac{0.5 - [PTIO]}{0.5} \times 100\% (2)$$

The parts and assembly of the flow cell used in this study are shown in **Figure 1**. The electrochemical performance of the symmetric PTIO flow battery, including redox reactions, CV curves, ESR validation of the symmetric design benefit, and flow cell cycling data, is shown in **Figure 2**. The feasibility validation for using FTIR as a suitable method to determine the SOC of the PTIO flow battery is shown in **Figure 3**. FTIR-based SOC determinations, including the voltage curve of the flow cell, the SOC obtained from FTIR and cross-validated by ESR, and a proposed online diagnostic system, are shown in **Figure 4**.



Figure 1: The photograph of the flow cell assembly. Please click here to view a larger version of this figure.



Figure 2: Electrochemical performance of PTIO. (a) the redox reactions of PTIO to PTIO⁺ (catholyte side) and to PTIO⁻ (anolyte side), respectively; (b) 500 cycles of almost completely overlapped CV curves of PTIO on a glassy carbon electrode; (c) ESR spectra showing the reaction between PTIO⁺ and PTIO⁻ regenerates the original PTIO; (d) cycling capacity and efficiency of the 0.5 M PTIO flow cell. This figure has been modified from reference²⁵. Please click here to view a larger version of this figure.



Figure 3: Feasibility validation for using FTIR to determine the SOC of the PTIO flow battery. (a) FTIR spectra of MeCN, 1.0 M TBAPF₆ in MeCN, and 0.5 M PTIO in 1.0 M TBAPF6 in MeCN; (b) FTIR spectra of PTIO, $PTIO^+$, and $PTIO^-$ (0.5 M in 1.0 M TBAPF6 in MeCN); (c) FTIR spectra of standard PTIO solutions at 0.05 M to 0.5 M with a 0.05 M interval. This figure has been modified from reference²⁵. Please click here to view a larger version of this figure.



Figure 4: FTIR-based SOC diagnostics. (a) the charging voltage curve of a 0.5 M PTIO flow cell showing five sample aliquots (#0, 1, 2, 3, 4) withdrawn from the cell during charging; (b) FTIR and (c) ESR spectra of the five catholyte sample aliquots; (d) unreacted PTIO concentrations and flow cell SOC obtained from FTIR measurements and cross-validated with ESR measurements; (e) a schematic of a flow battery device incorporated with online FTIR monitoring sensors. This figure has been modified from reference²⁵. Please click here to view a larger version of this figure.

| PTIO Conc. (M) | 0.05 | 0.1 | 0.15 | 0.2 | 0.25 | 0.3 | 0.35 | 0.4 | 0.45 | 0.5 |
|--------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| MeCN | 0.301 g | 0.295 g | 0.273 g | 0.25 g | 0.291 g | 0.255 g | 0.242 g | 0.232 g | 0.243 g | 0.263 g |
| TBAPF ₆ | 0.233 g | 0.233 g | 0.223 g | 0.21 g | 0.247 g | 0.222 g | 0.214 g | 0.213 g | 0.225 g | 0.255 g |
| PTIO | 0.007 g | 0.014 g | 0.02 g | 0.025 g | 0.037 g | 0.04 g | 0.045 g | 0.051 g | 0.061 g | 0.076 g |

Table 1: Compositions of the PTIO standard solutions.

Discussion

As we demonstrated before, ²⁵ FTIR is capable of non-invasively detecting the SOC of the PTIO flow battery. As a diagnostic tool, FTIR is particularly advantageous because of its easy accessibility, fast response, low cost, small space requirement, facility for online incorporation, no detector saturation, and the ability to correlate structural information to investigate molecular evolutions during flow battery operation. **Figure 3e** illustrates a proposed flow battery device integrating online FTIR sensors that enables real-time SOC monitoring for safe operations.

To better implement the protocol for electrochemical evaluation and FTIR-based SOC diagnostics, an air-free environment is essentially important; otherwise, the redox species at charged states will react with O_2 or moisture leading to material degradation and inaccurate SOC measurements. Strictly sealable FTIR cells must be used to avoid air contact with the electrolytes. In addition, because this technique is usable only for FTIR-sensitive redox materials, the feasibility validation through identifying well-distinguishable characteristic FTIR peaks is a critical step.

Considering the limited selectivity of battery membranes, redox material crossover is unavoidable for most flow batteries, which typically causes irreversible capacity fading. In this regard, the symmetric flow battery has the potential to overcome this drawback. In the PTIO flow battery, any crossover species will be converted to the original PTIO. Theoretically, the capacity loss caused by material crossover could be recovered by remixing the electrolytes, similar to vanadium flow batteries.³² Therefore, the symmetric battery design is promising to develop durable, reliable energy storage systems. The key limitation for the current PTIO system is that the PTIO⁻ (anolyte side) is not sufficiently stable due to gradually

occurring side reactions. Such a material loss explains the capacity fading observed in PTIO flow cells. Development of new ambipolar redox materials with high chemical stability in all oxidation states is the future direction to demonstrate the full potential of this battery design.

Disclosures

The authors have nothing to disclose.

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