A Protocol for Electrochemical Evaluations and State of Charge Diagnostics of A Symmetric Organic Redox Flow Battery
--Manuscript Draft--

Manuscript Number:	JoVE55171R2
Full Title:	A Protocol for Electrochemical Evaluations and State of Charge Diagnostics of A Symmetric Organic Redox Flow Battery
Article Type:	Methods Article - JoVE Produced Video
Keywords:	redox flow battery; nonaqueous; symmetric; organic; state of charge; FTIR
Manuscript Classifications:	92.23: Chemistry and Materials (General)
Corresponding Author:	Xiaoliang Wei Pacific Northwest National Laboratory Richland, WA UNITED STATES
Corresponding Author Secondary Information:	
Corresponding Author E-Mail:	Xiaoliang.Wei@pnnl.gov
Corresponding Author's Institution:	Pacific Northwest National Laboratory
Corresponding Author's Secondary Institution:	
First Author:	Xiaoliang Wei
First Author Secondary Information:	
Other Authors:	Wentao Duan, PhD
	Rama S Vemuri, PhD
	Dehong Hu
	Zheng Yang
Order of Authors Secondary Information:	
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, nonaqueous flow batteries have the potential to achieve high energy density because of the broad voltage windows of nonaqueous electrolytes. However, significant technical hurdles exist currently limiting nonaqueous 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 nonaqueous 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 cycling and offer reasonably accurate detection of the battery state of charge (SOC), as cross-validated by electron spin resonance (ESR) measurements. Herein we present a video protocol for the electrochemical evaluation and SOC diagnosis of the PTIO symmetric 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 safety and reliability in the field of non-aqueous redox flow batteries.
Author Comments:	

Additional Information:	
Question	Response
If this article needs to be "in-press" by a certain date, please indicate the date below and explain in your cover letter.	

TITLE:

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

AUTHORS:
Wentao Duan[§], Rama S. Vemuri[§], Dehong Hu, Zheng Yang, Xiaoliang Wei

[§] Equal contribution

Dr. Wentao Duan
[1] Joint Center for Energy Storage Research (JCESR)
[2] Energy & Environment Directorate
 Pacific Northwest National Laboratory
 Richland, WA, USA
 Wentao.Duan@pnnl.gov

Dr. Rama S. Vemuri
[1] Joint Center for Energy Storage Research (JCESR)
[2] Earth & Biological Systems Directorate
 Pacific Northwest National Laboratory
 Richland, WA, USA
 Rama.Vemuri@pnnl.gov

Dr. Dehong Hu
 Earth & Biological Systems Directorate
 Pacific Northwest National Laboratory
 Richland, WA, USA
 Dehong.Hu@pnnl.gov

Dr. Zheng Yang
[1] Joint Center for Energy Storage Research (JCESR)
[2] Physical & Computational Sciences Directorate
 Pacific Northwest National Laboratory
 Richland, WA, USA
 Zheng.Yang@pnnl.gov

Dr. Xiaoliang Wei
[1] Joint Center for Energy Storage Research (JCESR)
[2] Energy & Environment Directorate
 Pacific Northwest National Laboratory
 Richland, WA, USA
 Xiaoliang.Wei@pnnl.gov

CORRESPONDING AUTHOR:

Xiaoliang Wei (Xiaoliang.Wei@pnnl.gov)

KEYWORDS:
redox flow battery, nonaqueous, symmetric, organic, state of charge, FTIR

SHORT ABSTRACT:
We present the protocols for electrochemically evaluating a symmetric nonaqueous organic redox flow battery and for diagnosing its state of charge using FTIR.

LONG 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, nonaqueous flow batteries have the potential to achieve high energy density because of the broad voltage windows of nonaqueous electrolytes. However, significant technical hurdles exist currently limiting nonaqueous 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 nonaqueous 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 cycling and offer reasonably accurate detection of the battery state of charge (SOC), as cross-validated by electron spin resonance (ESR) measurements. Herein we present a video protocol for the electrochemical evaluation and SOC diagnosis of the PTIO symmetric 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.

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.[1-3] Traditional aqueous flow batteries suffer from limited energy density, mostly due to the narrow voltage window to avoid water electrolysis.[4-8] In contrast, nonaqueous 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.[16-19]

However, the potential of nonaqueous 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 nonaqueous flow cells. Second, the rate capability of nonaqueous 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 nonaqueous 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 nonaqueous 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.[22-24]

We have recently introduced a novel symmetric nonaqueous flow battery design based on a new ambipolar redox material, 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (PTIO).[25] This flow battery holds the promise to address the aforementioned challenges of nonaqueous 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
1.1) CV Test
1.1.1) 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.

1.1.2) Dissolve silver nitrate (8.5 mg) with MeCN (5 mL) in the glove box, *i.e.*, 10 mM $AgNO_3$. Add the solution into the glass tube of a silver/silver nitrate reference electrode.

1.1.3) 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.

1.1.4) Dissolve PTIO (52 mg) and tetrabutylammonium hexafluorophosphate ($TBAPF_6$, 0.87 g) in MeCN (1.10 g), *i.e.*, 0.1 M PTIO/1.0 M $TBAPF_6$. Add the solution to the flask to submerge the tips of the three electrodes.

1.1.5) 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.

1.2) Flow Cell Assembly
1.2.1) Cut the graphite felts to an area of 1 x 10 cm^2 using a razor blade. Similarly, cut a porous separator to an area of 3 x 12 cm^2.

1.2.2) 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.

1.2.3) 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.

1.3 Demonstration of Symmetric Cell Benefit
1.3.1) Assemble the flow cell according to Section 1.2. Dissolve PTIO (10 mg) and $TBAPF_6$ (3.3 g) with MeCN (4.4 g) in the glove box, *i.e.*, 5.0 mM PTIO/1.0 M $TBAPF_6$. 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.

1.3.2) 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/cm^2 until the voltage reached 1.9 V. Stop the charging. Pump out the electrolytes into the glass vials.

1.3.3) 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.

1.3.4) Measure electron spin resonance (ESR) spectrum of the above four electrolytes.[25]

1.3.4.1) 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).

1.3.4.2) Mount the ESR tubing to an ESR spectrometer fitted with an SHQE resonator with microwave frequency ~9.85 GHz (X band).

1.3.4.3) Collect the ESR spectrum for the four electrolytes in Section 1.3.3.

1.4) Flow Cell Test
1.4.1) Assemble a flow cell following Section 1.2.

1.4.2) Dissolve PTIO (1.05 g) and TBAPF$_6$ (3.50 g) with MeCN (3.60 g) in the glove box, *i.e.,* 0.5 M PTIO/1.0 M TBAPF$_6$. Add 4 mL of the solution to each glass vial. Flow the electrolytes at 20 mL/min.

1.4.3) 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.

1.4.4) 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
2.1) FTIR Feasibility Validation
2.1.1) Prepare the following three electrolyte solutions in the glove box: (a) MeCN (0.50 g); (b) TBAPF$_6$ (0.23 g) with MeCN (0.30 g), *i.e.,* 1.0 M TBAPF$_6$; (c) PTIO (75 mg) and TBAPF$_6$ (0.25 g) with MeCN (0.26 g), *i.e.,* 0.5 M PTIO/1.0 M TBAPF$_6$.

2.1.2) Measure FTIR for the three electrolyte solutions.

2.1.2.1) 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.

2.1.2.2) Put the FTIR cell into a storage container and transfer it out of the glove box.

2.1.2.3) Quickly mount the FTIR cell to a spectrometer and collect the FTIR spectrum.

2.1.3) Assemble a flow cell following Section 1.2.

2.1.4) Dissolve PTIO (1.05 g) and TBAPF$_6$ (3.50 g) with MeCN (3.60 g) in the glove box, *i.e.*, 0.5 M PTIO/1.0 M TBAPF$_6$. Add 4 mL of the solution to each glass vial. Flow the electrolytes at 20 mL/min.

2.1.5) Fully charge the flow cell until the voltage reaches 2.2 V. Stop the charging and the pump.

2.1.6) Measure the FTIR spectra for both the positive and negative electrolytes, respectively, following the procedure in Section 2.1.2.

2.1.7) Prepare a series of PTIO solutions (0.05 - 0.5 M) in 1.0 M TBAPF$_6$ in MeCN in the glove box with the compositions in Table 1.

2.1.8) Measure the FTIR spectrum for each of the solutions in Section 2.1.6, following the procedure in Section 2.1.2.

2.2) FTIR Measurement of SOC
2.2.1) Assemble a flow cell following Section 1.2.

2.2.2) Dissolve PTIO (2.9 g) and TBAPF$_6$ (9.6 g) with MeCN (9.8 g) in the glove box, *i.e.*, 0.5 M PTIO/1.0 M TBAPF$_6$. Add 11 mL of the solution to each of the two glass vials. Flow the electrolytes at 20 mL/min.

2.2.2) Charge the flow cell at a constant current of 10 mA/cm² at a flow rate of 20 mL/min.

2.2.3) At the charge time of 0, 18, 36, 54, and 72 minutes, 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.

2.2.4) Measure the FTIR spectrum for the above five sample aliquots, following the procedure in Section 2.1.2.

2.2.5) 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 cm^2 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 nonaqueous RFBs, which cycled typically near 0.1 M concentrations, with current densities less than 0.5 mA/cm^2, and/or EEs no higher than 50%.[27-30]

FTIR has successfully validated its qualifications as a suitable SOC-diagnosing tool for the PTIO flow battery, because of the characteristic FTIR peak at 1218 cm^{-1} that presumably corresponds to the N-O bond.[31] First, the supporting MeCN solvent and TBAPF$_6$ 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:

$$-\log(T) = 1.11[\text{PTIO}] + 0.156$$

(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 1218 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 1218 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

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 Ref. 25.

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 Ref. 25.

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 Ref. 25.

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.

REFERENCES
(1)   Dunn, B., Kamath, H., Tarascon, J. M. Electrical Energy Storage for the Grid: A Battery of Choices. *Science* **334** (6058), 928-935, DOI: 10.1126/science.1212741 (2011).
(2)   Yang, Z. G., *et al*. Electrochemical Energy Storage for Green Grid. *Chem. Rev.* **111** (5), 3577-3613, DOI 10.1021/Cr100290v (2011).
(3)   Wang, W., Luo, Q., Li, B., Wei, X., Li, L., Yang, Z. Recent Progress in Redox Flow Battery Research and Development. *Adv. Funct. Mater.* **23** (8), 970-986, DOI: 10.1002/adfm.201200694 (2013).
(4)   Skyllas-Kazacos, M.; Chakrabarti, M. H.; Hajimolana, S. A.; Mjalli, F. S.; Saleem, M. Progress in Flow Battery Research and Development. *J. Electrochem. Soc.* **158** (8), R55-R79, DOI:

10.1149/1.3599565 (2011).

(5)   Weber, A. Z., *et al*. Redox Flow Batteries: A Review. *J. Appl. Electrochem.* **41** (10), 1137-1164, DOI: 10.1007/s10800-011-0348-2 (2011).

(6)   Noack, J., Roznyatovskaya, N., Herr, T., Fischer, P. The Chemistry of Redox-Flow Batteries. *Angew. Chem. Int. Ed.* **54** (34), 9775-9808, DOI: 10.1002/anie.201410823 (2015)

(7)   Soloveichik, G. L. Flow Batteries: Current Status and Trends. *Chem. Rev.* **115** (20), 11533-11558, DOI: 10.1021/cr500720t (2015).

(8)   Leung, P.; Li, X., de Leon, C. P., Berlouis, L., Low, C. T. J., Walsh, F. C. Progress in Redox Flow Batteries, Remaining Challenges and Their Applications in Energy Storage. *RSC Adv.* **2** (27), 10125-10156, DOI: 10.1039/C2ra21342g (2012).

(9)   Gong, K., Fang, Q., Gu, S., Li, S., Yan, Y. Nonaqueous Redox-Flow Batteries: Organic Solvents, Supporting Electrolytes, and Redox Pairs. *Energy Environ. Sci.* **8** (12), 3515-3530, DOI: 10.1039/c5ee02341f (2015).

(10)   Shin, S. H., Yun, S. H., Moon, S. H. A Review of Current Developments in Non-aqueous Redox Flow Batteries: Characterization of Their Membranes for Design Perspective. *RSC Adv.* **3** (24), 9095-9116, DOI: 10.1039/c3ra00115f (2013).

(11)   Cappillino, P. J., *et al*. Application of Redox Non-Innocent Ligands to Non-Aqueous Flow Battery Electrolytes. *Adv. Energy Mater.* **4** (1), 1300566, DOI: 10.1002/Aenm.201300566 (2014).

(12)   Suttil, J. A. *et al*, Metal Acetylacetonate Complexes for High Energy Density Non-aqueous Redox Flow Batteries. *J. Mater. Chem. A* **3** (15), 7929-7938, DOI: 10.1039/c4ta06622g (2015).

(13)   Brushett, F. R., Vaughey, J. T., Jansen, A. N. An All-Organic Non-aqueous Lithium-Ion Redox Flow Battery. *Adv. Energy Mater.* **2** (11), 1390-1396, DOI 10.1002/aenm.201200322 (2012).

(14)   Wei, X., *et al*, Radical Compatibility with Nonaqueous Electrolytes and Its Impact on an All-Organic Redox Flow Battery. *Angew. Chem. Int. Ed.* **54** (30), 8684-8687, DOI: 10.1002/anie.201501443 (2015).

(15)   Nagarjuna, G. *et al*, Impact of Redox-Active Polymer Molecular Weight on the Electrochemical Properties and Transport Across Porous Separators in Nonaqueous Solvents. *J. Am. Chem. Soc.* **136** (46), 16309-16316, DOI: 10.1021/Ja508482e (2014).

(16)   Wei, X. *et al*, TEMPO-Based Catholyte for High-Energy Density Nonaqueous Redox Flow Batteries. *Adv. Mater.* **26** (45), 7649–7653, DOI: 10.1002/adma.201403746 (2014).

(17)   Wei, X. *et al*, Towards High-Performance Nonaqueous Redox Flow Electrolyte Via Ionic Modification of Active Species. *Adv. Energy Mater.* **5** (1), 1400678, DOI: 10.1002/aenm.201400678 (2015).

(18)   Fan, F. Y. *et al*, Polysulfide Flow Batteries Enabled by Percolating Nanoscale Conductor Networks. *Nano Lett.* **14** (4), 2210-2218, DOI: 10.1021/Nl500740t (2014).

(19)   Pan, H. *et al*, On the Way Toward Understanding Solution Chemistry of Lithium Polysulfides for High Energy Li-S Redox Flow Batteries. *Adv. Energy Mater.* **5** (16), 1500113, DOI: 10.1002/aenm.201500113 (2015).

(20)   Escalante-Garcia, I. L., Wainright, J. S., Thompson, L. T., Savinell, R. F. Performance of a Non-Aqueous Vanadium Acetylacetonate Prototype Redox Flow Battery: Examination of Separators and Capacity Decay. *J. Electrochem. Soc.* **162** (3), A363-A372, DOI:

10.1149/2.0471503jes (2015).

(21)   Wei, X. *et al*, Microporous Separators for Fe/V Redox Flow Batteries. *J. Power Sources* **218**, 39-45, DOI 10.1016/j.jpowsour.2012.06.073 (2012).

(22)   Skyllas-Kazacos, M., Kazacos, M. State of Charge Monitoring Methods for Vanadium Redox Flow Battery Control. *J. Power Sources* **196** (20), 8822-8827, DOI: 10.1016/j.jpowsour.2011.06.080 (2011).

(23)   Brooker, R. P., Bell, C. J., Bonville, L. J., Kunz, H. R., Fenton, J. M. Determining Vanadium Concentrations Using the UV-Vis Response Method. *J. Electrochem. Soc.* **162** (4), A608-A613, DOI: 10.1149/2.0371504jes (2015).

(24)   Petchsingh, C. et al, Spectroscopic Measurement of State of Charge in Vanadium Flow Batteries with an Analytical Model of VIV-VV Absorbance. *J. Electrochem. Soc.* **163** (1), A5068-A5083, DOI: 10.1149/2.0091601jes (2016).

(25)   Duan, W. *et al*, A Symmetric Organic-Based Nonaqueous Redox Flow Battery and Its State of Charge Diagnostics by FTIR. *J. Mater. Chem. A* **4** (15), 5448-5456, DOI: 10.1039/c6ta01177b (2016).

(26)   Potash, R. A., McKone, J. R., Conte, S., Abruña, H. D. On the Benefits of a Symmetric Redox Flow Battery. *J. Electrochem. Soc.* **163** (3), A338-A344, DOI: 10.1149/2.0971602jes (2016).

(27)   Kim, H. S. *et al*, A Tetradentate Ni(II) Complex Cation as a Single Redox Couple for Non-aqueous Flow Batteries. *J. Power Sources* **283** 300-304, DOI: 10.1016/j.jpowsour.2015.02.083 (2015).
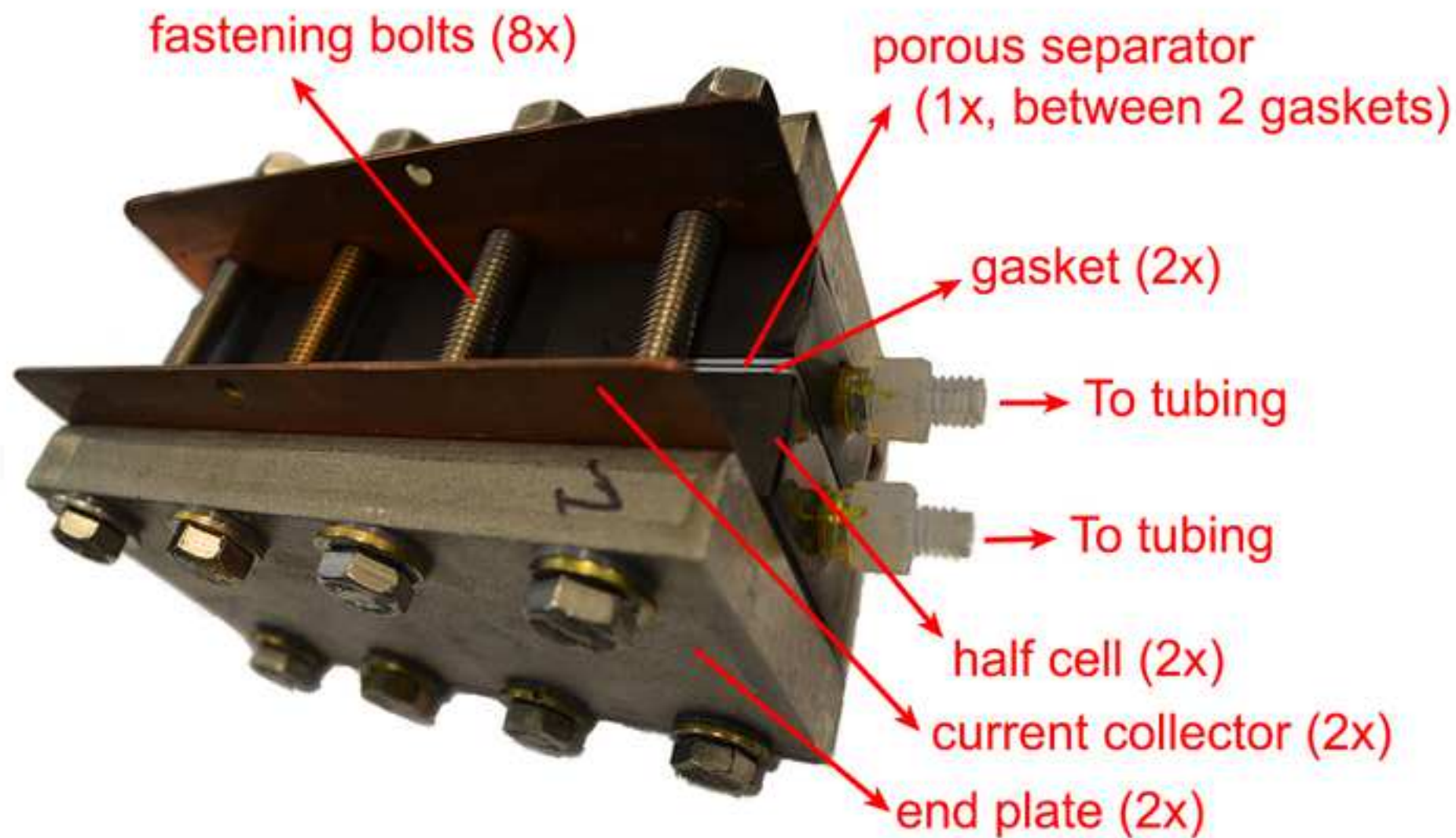
(28)   Shinkle, A. A., Sleightholme, A. E. S., Griffith, L. D., Thompson, L. T., Monroe, C. W. Degradation Mechanisms in The Non-aqueous Vanadium Acetylacetonate Redox Flow Battery. *J. Power Sources* **206**, 490-496, DOI: 10.1016/j.jpowsour.2010.12.096 (2012).

(29)   Li, Z. *et al*, Electrochemical Properties of an All-Organic Redox Flow Battery Using 2,2,6,6-Tetramethyl-1-Piperidinyloxy and N-Methylphthalimide. *Electrochem. Solid-State Lett.* **14** (12), A171-A173, DOI: 10.1149/2.012112esl (2011).

(30)   Schaltin, S. *et al*, Towards an All-Copper Redox Flow Battery Based on a Copper-Containing Ionic Liquid. *Chem. Commun.* **52** , 414-417, DOI: 10.1039/C5CC06774J (2016).

(31)   SDBS, http://sdbs.db.go.jp, accessed on January 7, 2016.

(32)   Luo, Q. *et al*, Capacity Decay and Remediation of Nafion-based All-Vanadium Redox Flow Batteries. *ChemSusChem* **6** (2), 268-274, DOI: 10.1002/cssc.201200730 (2013).
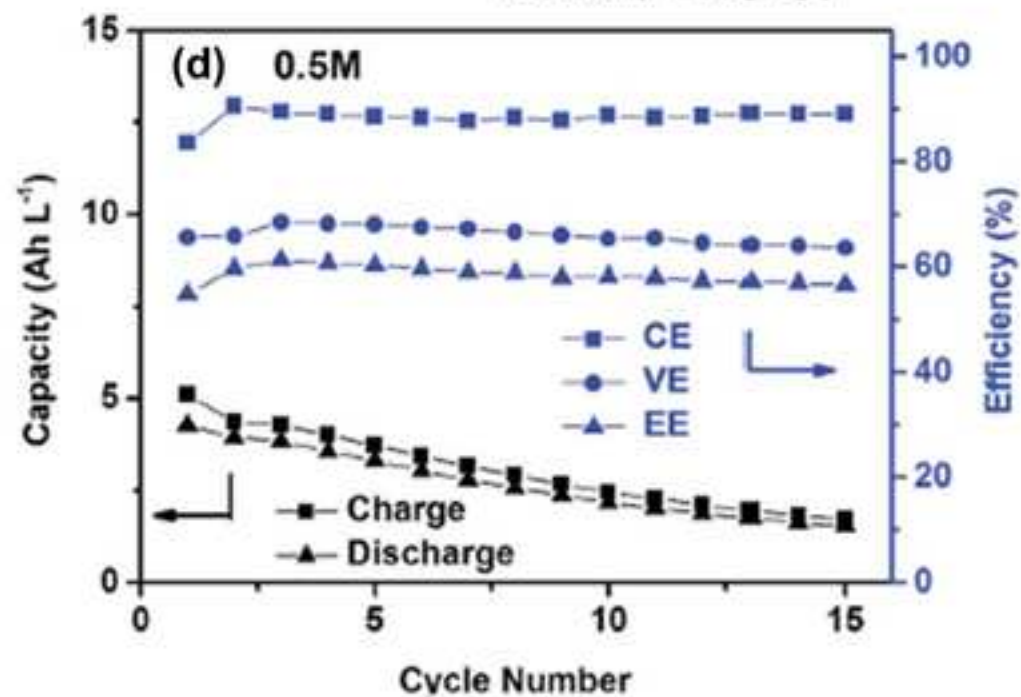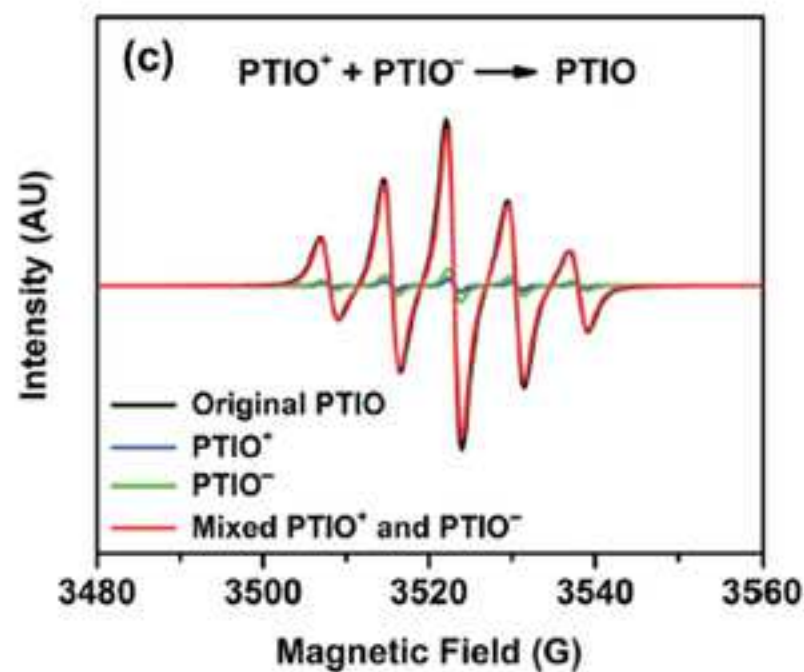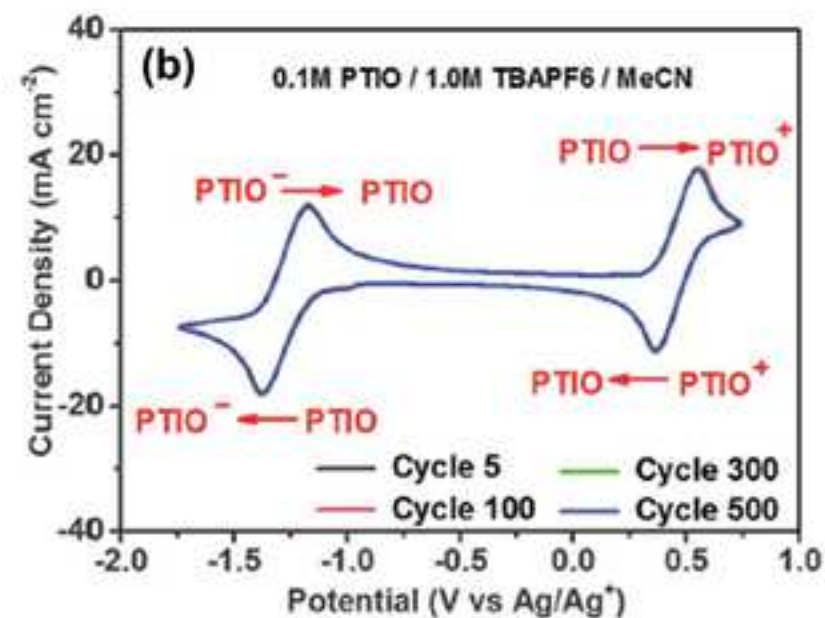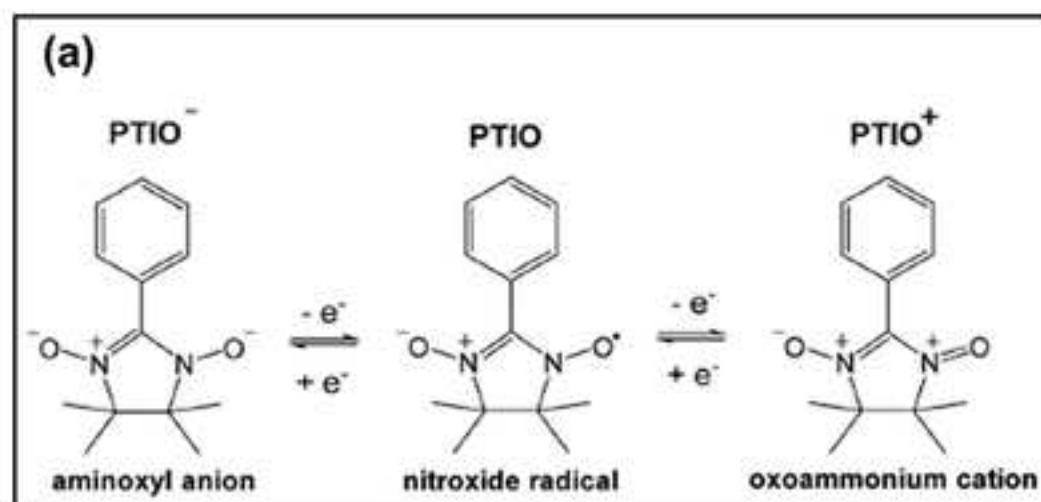
Figure 1

fastening bolts (8x)

porous separator
(1x, between 2 gaskets)

gasket (2x)

→ To tubing

→ To tubing

half cell (2x)

current collector (2x)

end plate (2x)

Figure 3

Figure 4　　　　　　　　　　　　　　　　　　　　　　　　　　Click here to download Figure Figure4_FTIR_SOC_R2.tif ⬇
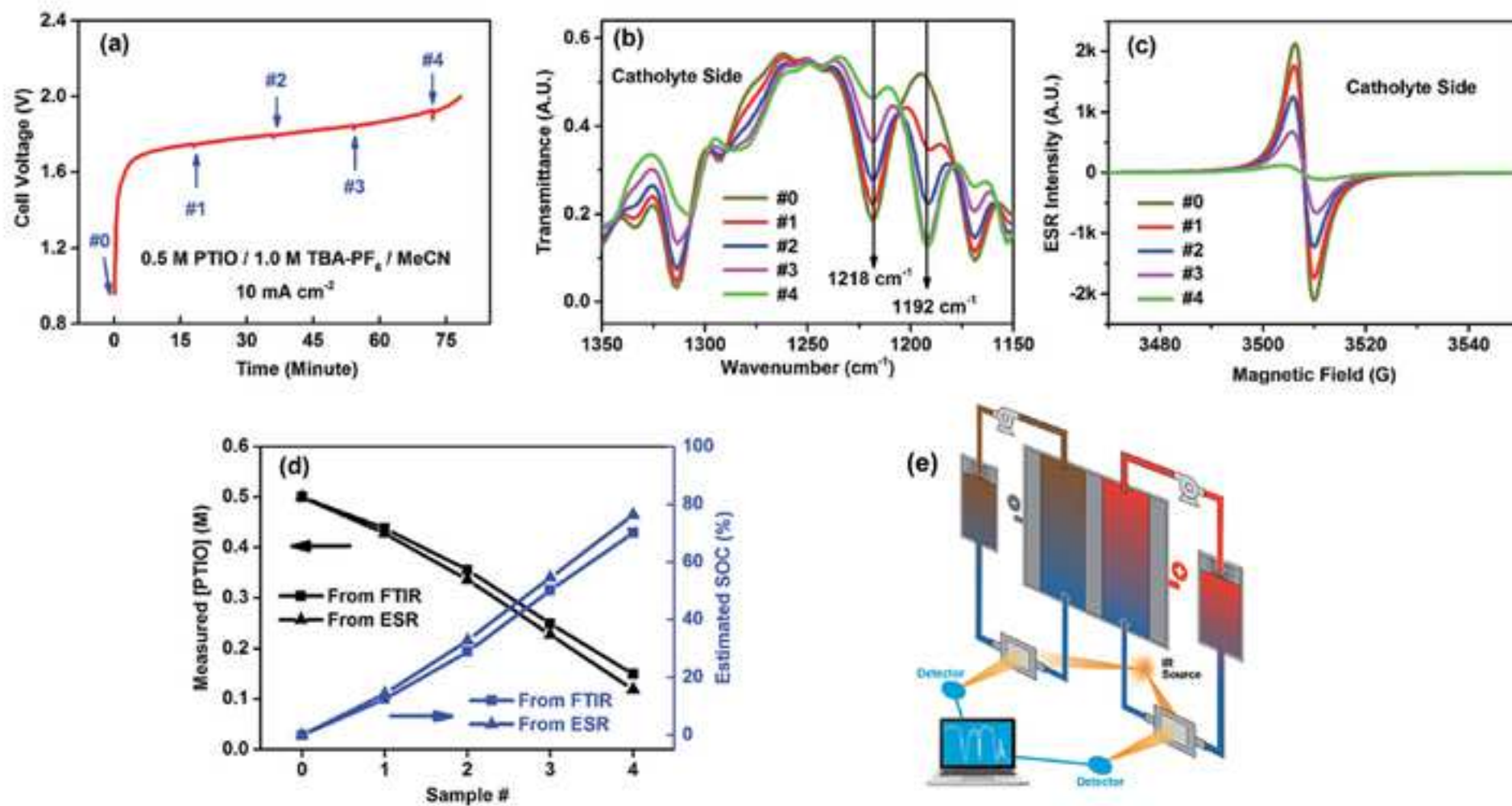
Table 1

PTIO Conc. (M)	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4	0.45
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
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
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

0.5

0.263 g
0.255 g
0.076 g

Name of Material/ Equipment	Company	Catalog Number	Comments/Description
PTIO	TCI America	A5440	>98.0%
Tetrabutylammonium hexafluorophosphate	Sigma-Aldrich	86879	electrochemical grade, ≥99.0%
MeCN	BASF	50325685	Battery grade
Silver nitrate	Sigma-Aldrich	204390	99.9999% trace metals basis
Gamma alumina powder	CH Instruments	CHI120	
Graphite felt	SGL	GFD3	Vacuum-dry at 70°C for 24 h
Porous separator	Daramic	AA800	Vacuum-dry at 70°C for 24 h
Battery Tester	Wuhan LAND electro	Lanhe	1A current range
Electrochemical Workstation	Solartron Analytical	ModuLab	
glove box	MBRAUN	Labmaster SP	oxygen and water levels <1 ppm
ESR spectrometer	Bruker	Elexsys 580	Equipped with an SHQE resonator with microwave frequency ~9.85 GHz (X band) at 2 mW power, with 100 kHz field modulation

jove
JOURNAL OF
VISUALIZED EXPERIMENTS

1 Alewife Center #200
Cambridge, MA 02140
tel. 617.945.9051
www.jove.com

ARTICLE AND VIDEO LICENSE AGREEMENT

Title of Article:

Electrochemical Evaluation and FTIR-Based State of Charge Diagnostics of A PTIO-Based Symmetric Nonaqueous Redox Flow Battery

Author(s):

Wentao Duan, Rama Vemuri, Dehong Hu, Zheng Yang, Xiaoliang Wei

Item 1 (check one box): The Author elects to have the Materials be made available (as described at http://www.jove.com/publish) via: [X] Standard Access [ ] Open Access

Item 2 (check one box):

[X] The Author is NOT a United States government employee.

[ ] The Author is a United States government employee and the Materials were prepared in the course of his or her duties as a United States government employee.

[ ] The Author is a United States government employee but the Materials were NOT prepared in the course of his or her duties as a United States government employee.

ARTICLE AND VIDEO LICENSE AGREEMENT

1. Defined Terms. As used in this Article and Video License Agreement, the following terms shall have the following meanings: "**Agreement**" means this Article and Video License Agreement; "**Article**" means the article specified on the last page of this Agreement, including any associated materials such as texts, figures, tables, artwork, abstracts, or summaries contained therein; "**Author**" means the author who is a signatory to this Agreement; "**Collective Work**" means a work, such as a periodical issue, anthology or encyclopedia, in which the Materials in their entirety in unmodified form, along with a number of other contributions, constituting separate and independent works in themselves, are assembled into a collective whole; "**CRC License**" means the Creative Commons Attribution-Non Commercial-No Derivs 3.0 Unported Agreement, the terms and conditions of which can be found at: http://creativecommons.org/licenses/by-nc-nd/3.0/legalcode; "**Derivative Work**" means a work based upon the Materials or upon the Materials and other pre-existing works, such as a translation, musical arrangement, dramatization, fictionalization, motion picture version, sound recording, art reproduction, abridgment, condensation, or any other form in which the Materials may be recast, transformed, or adapted; "**Institution**" means the institution, listed on the last page of this Agreement, by which the Author was employed at the time of the creation of the Materials; "**JoVE**" means MyJove Corporation, a Massachusetts corporation and the publisher of *The Journal of Visualized Experiments;* "**Materials**" means the Article and / or the Video; "**Parties**" means the Author and JoVE; "**Video**" means any video(s) made by the Author, alone or in conjunction with any other parties, or by JoVE or its affiliates or agents, individually or in collaboration with the Author or any other parties, incorporating all or any portion of the Article, and in which the Author may or may not appear.

2. Background. The Author, who is the author of the Article, in order to ensure the dissemination and protection of the Article, desires to have the JoVE publish the Article and create and transmit videos based on the Article. In furtherance of such goals, the Parties desire to memorialize in this Agreement the respective rights of each Party in and to the Article and the Video.

3. Grant of Rights in Article. In consideration of JoVE agreeing to publish the Article, the Author hereby grants to JoVE, subject to **Sections 4** and **7** below, the exclusive, royalty-free, perpetual (for the full term of copyright in the Article, including any extensions thereto) license (a) to publish, reproduce, distribute, display and store the Article in all forms, formats and media whether now known or hereafter developed (including without limitation in print, digital and electronic form) throughout the world, (b) to translate the Article into other languages, create adaptations, summaries or extracts of the Article or other Derivative Works (including, without limitation, the Video) or Collective Works based on all or any portion of the Article and exercise all of the rights set forth in (a) above in such translations, adaptations, summaries, extracts, Derivative Works or Collective Works and (c) to license others to do any or all of the above. The foregoing rights may be exercised in all media and formats, whether now known or hereafter devised, and include the right to make such modifications as are technically necessary to exercise the rights in other media and formats. If the "Open Access" box has been checked in **Item 1** above, JoVE and the Author hereby grant to the public all such rights in the Article as provided in, but subject to all limitations and requirements set forth in, the CRC License.

1

612542.6

4. Retention of Rights in Article. Notwithstanding the exclusive license granted to JoVE in **Section 3** above, the Author shall, with respect to the Article, retain the non-exclusive right to use all or part of the Article for the non-commercial purpose of giving lectures, presentations or teaching classes, and to post a copy of the Article on the Institution's website or the Author's personal website, in each case provided that a link to the Article on the JoVE website is provided and notice of JoVE's copyright in the Article is included. All non-copyright intellectual property rights in and to the Article, such as patent rights, shall remain with the Author.

5. Grant of Rights in Video – Standard Access. This **Section 5** applies if the "Standard Access" box has been checked in **Item 1** above or if no box has been checked in **Item 1** above. In consideration of JoVE agreeing to produce, display or otherwise assist with the Video, the Author hereby acknowledges and agrees that, Subject to **Section 7** below, JoVE is and shall be the sole and exclusive owner of all rights of any nature, including, without limitation, all copyrights, in and to the Video. To the extent that, by law, the Author is deemed, now or at any time in the future, to have any rights of any nature in or to the Video, the Author hereby disclaims all such rights and transfers all such rights to JoVE.

6. Grant of Rights in Video – Open Access. This **Section 6** applies only if the "Open Access" box has been checked in **Item 1** above. In consideration of JoVE agreeing to produce, display or otherwise assist with the Video, the Author hereby grants to JoVE, subject to **Section 7** below, the exclusive, royalty-free, perpetual (for the full term of copyright in the Article, including any extensions thereto) license (a) to publish, reproduce, distribute, display and store the Video in all forms, formats and media whether now known or hereafter developed (including without limitation in print, digital and electronic form) throughout the world, (b) to translate the Video into other languages, create adaptations, summaries or extracts of the Video or other Derivative Works or Collective Works based on all or any portion of the Video and exercise all of the rights set forth in (a) above in such translations, adaptations, summaries, extracts, Derivative Works or Collective Works and (c) to license others to do any or all of the above. The foregoing rights may be exercised in all media and formats, whether now known or hereafter devised, and include the right to make such modifications as are technically necessary to exercise the rights in other media and formats. For any Video to which this Section 6 is applicable, JoVE and the Author hereby grant to the public all such rights in the Video as provided in, but subject to all limitations and requirements set forth in, the CRC License.

7. Government Employees. If the Author is a United States government employee and the Article was prepared in the course of his or her duties as a United States government employee, as indicated in **Item 2** above, and any of the licenses or grants granted by the Author hereunder exceed the scope of the 17 U.S.C. 403, then the rights granted hereunder shall be limited to the maximum rights permitted under such statute. In such case, all provisions contained herein that are not in conflict with such statute shall remain in full force and effect, and all provisions contained herein that do so conflict shall be deemed to be amended so as to provide to JoVE the maximum rights permissible within such statute.

8. Likeness, Privacy, Personality. The Author hereby grants JoVE the right to use the Author's name, voice, likeness, picture, photograph, image, biography and performance in any way, commercial or otherwise, in connection with the Materials and the sale, promotion and distribution thereof. The Author hereby waives any and all rights he or she may have, relating to his or her appearance in the Video or otherwise relating to the Materials, under all applicable privacy, likeness, personality or similar laws.

9. Author Warranties. The Author represents and warrants that the Article is original, that it has not been published, that the copyright interest is owned by the Author (or, if more than one author is listed at the beginning of this Agreement, by such authors collectively) and has not been assigned, licensed, or otherwise transferred to any other party. The Author represents and warrants that the author(s) listed at the top of this Agreement are the only authors of the Materials. If more than one author is listed at the top of this Agreement and if any such author has not entered into a separate Article and Video License Agreement with JoVE relating to the Materials, the Author represents and warrants that the Author has been authorized by each of the other such authors to execute this Agreement on his or her behalf and to bind him or her with respect to the terms of this Agreement as if each of them had been a party hereto as an Author. The Author warrants that the use, reproduction, distribution, public or private performance or display, and/or modification of all or any portion of the Materials does not and will not violate, infringe and/or misappropriate the patent, trademark, intellectual property or other rights of any third party. The Author represents and warrants that it has and will continue to comply with all government, institutional and other regulations, including, without limitation all institutional, laboratory, hospital, ethical, human and animal treatment, privacy, and all other rules, regulations, laws, procedures or guidelines, applicable to the Materials, and that all research involving human and animal subjects has been approved by the Author's relevant institutional review board.

10. JoVE Discretion. If the Author requests the assistance of JoVE in producing the Video in the Author's facility, the Author shall ensure that the presence of JoVE employees, agents or independent contractors is in accordance with the relevant regulations of the Author's institution. If more than one author is listed at the beginning of this Agreement, JoVE may, in its sole discretion, elect not take any action with respect to the Article until such time as it has received complete, executed Article and Video License Agreements from each such author. JoVE reserves the right, in its absolute and sole discretion and without giving any reason therefore, to accept or decline any work submitted to JoVE. JoVE and its employees, agents and independent contractors shall have

jove

JOURNAL OF
VISUALIZED EXPERIMENTS

1 Alewife Center #200
Cambridge, MA 02140
tel. 617.945.9051
www.jove.com

ARTICLE AND VIDEO LICENSE AGREEMENT

full, unfettered access to the facilities of the Author or of the Author's institution as necessary to make the Video, whether actually published or not. JoVE has sole discretion as to the method of making and publishing the Materials, including, without limitation, to all decisions regarding editing, lighting, filming, timing of publication, if any, length, quality, content and the like.

11. <u>Indemnification</u>. The Author agrees to indemnify JoVE and/or its successors and assigns from and against any and all claims, costs, and expenses, including attorney's fees, arising out of any breach of any warranty or other representations contained herein. The Author further agrees to indemnify and hold harmless JoVE from and against any and all claims, costs, and expenses, including attorney's fees, resulting from the breach by the Author of any representation or warranty contained herein or from allegations or instances of violation of intellectual property rights, damage to the Author's or the Author's institution's facilities, fraud, libel, defamation, research, equipment, experiments, property damage, personal injury, violations of institutional, laboratory, hospital, ethical, human and animal treatment, privacy or other rules, regulations, laws, procedures or guidelines, liabilities and other losses or damages related in any way to the submission of work to JoVE, making of videos by JoVE, or publication in *JoVE* or elsewhere by JoVE. The Author shall be responsible for, and shall hold JoVE harmless from, damages caused by lack of sterilization, lack of cleanliness or by contamination due to the making of a video by JoVE its employees, agents or independent contractors. All sterilization, cleanliness or decontamination procedures shall be solely the responsibility of the Author and shall be undertaken at the Author's

expense. All indemnifications provided herein shall include JoVE's attorney's fees and costs related to said losses or damages. Such indemnification and holding harmless shall include such losses or damages incurred by, or in connection with, acts or omissions of JoVE, its employees, agents or independent contractors.

12. <u>Fees</u>. To cover the cost incurred for publication, JoVE must receive payment before production and publication the Materials. Payment is due in 21 days of invoice. Should the Materials not be published due to an editorial or production decision, these funds will be returned to the Author. Withdrawal by the Author of any submitted Materials after final peer review approval will result in a US$1,200 fee to cover pre-production expenses incurred by JoVE. If payment is not received by the completion of filming, production and publication of the Materials will be suspended until payment is received.

13. <u>Transfer, Governing Law</u>. This Agreement may be assigned by JoVE and shall inure to the benefits of any of JoVE's successors and assignees. This Agreement shall be governed and construed by the internal laws of the Commonwealth of Massachusetts without giving effect to any conflict of law provision thereunder. This Agreement may be executed in counterparts, each of which shall be deemed an original, but all of which together shall be deemed to me one and the same agreement. A signed copy of this Agreement delivered by facsimile, e-mail or other means of electronic transmission shall be deemed to have the same legal effect as delivery of an original signed copy of this Agreement.

A signed copy of this document must be sent with all new submissions. Only one Agreement required per submission.
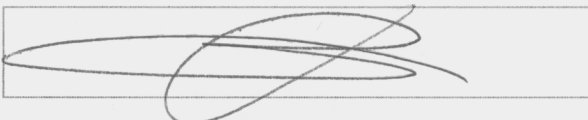
CORRESPONDING AUTHOR:

Name: Xiaoliang Wei

Department: Energy & Environmet Directorate

Institution: Pacific Northwest National Laboratory

Article Title: Electrochemical Evaluation and FTIR-Based State of Charge Diagnostics of A PTIO-Based Symmetric Nonaqueous Redox Flow Battery

Signature: Date: 06/28/16

Please submit a <u>signed</u> and <u>dated</u> copy of this license by one of the following three methods:
1) Upload a scanned copy of the document as a pfd on the JoVE submission site;
2) Fax the document to +1.866.381.2236;
3) Mail the document to JoVE / Attn: JoVE Editorial / 1 Alewife Center #200 / Cambridge, MA 02139

For questions, please email submissions@jove.com or call +1.617.945.9051

612542.6

<u>Response to Reviewers and Editorial Comments on</u>

"Electrochemical Performance and State of Charge Diagnostics of A Symmetric Organic Redox Flow Battery " (Manuscript Number: JoVE55171)

We would like to take this opportunity to thank the Editor and the reviewers for their comments and suggestions. We have incorporated the reviewers' corrections into the revised manuscript, and the details of our responses are given below.

1. Answers to the Editorial Comments

The manuscript has been modified by the Science Editor to comply with the JoVE formatting standard. Please maintain the current formatting throughout the manuscript. The updated manuscript (55171_R1_071316.docx) is located in your Editorial Manager account. In the revised PDF submission, there is a hyperlink for downloading the .docx file. Please download the .docx file and use this updated version for any future revisions.

Response: We revised the title to "A Protocol for Electrochemical Evaluations and State of Charge Diagnostics of A Symmetric Organic Redox Flow Battery", in order to better reflect the content.

1. Grammar:
-Line 64 – "This redox materials"
-Line 313 – "highly viable"
-Line 315 – "high facileness"

Response: These grammatical errors have been corrected.

2. Visualization: Please include a photograph of the flow cell as a supplementary file.

Response: A photograph of the parts and assembly of the flow cell used in this study was added as a new Figure 1, which is copied here for easy review. The figure numbers of the other figures were changed accordingly.
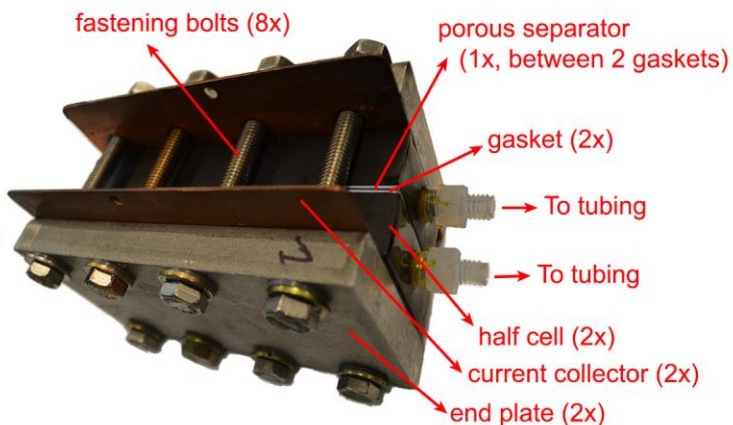
"

fastening bolts (8x)

porous separator
(1x, between 2 gaskets)

gasket (2x)

→ To tubing

→ To tubing

half cell (2x)

current collector (2x)

end plate (2x)

Figure 1: The photograph of the flow cell assembly
"

3. Additional detail is required:
-1.1.5 – Are any of the electrodes submerged in the solution?

Response: A phrase of "to submerge the tips of the three electrodes" was added to indicate this setup.

-1.2.1 – How are they cut?

Response: The sentence was revised to show the cutting method: "Cut the graphite felts to an area of 1 x 10 cm^2 using a razor blade. Similarly, cut a porous separator to an area of 3 x 12 cm^2."

-1.2.2 – How is the flow cell assembled? Please describe.

Response: A flow cell assembling step was added as the new 1.2.3), which is also copied here for easy review.

"1.2.3) 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. "

-1.2.4 – How is the flow cell charged? What actions need to be performed for this? From where are positive and negative electrolytes collected? What distinguishes them?

Response: Experimental details were added to this step to address these questions, which are copied below for easy review.

"1.3.2) Connect the positive and negative current collectors of the flow cell to the battery

tester. Charge the flow cell at a constant current of 5 mA/cm^2 until the voltage reached 1.9 V. Stop the charging. Pump out the electrolytes into the glass vials."

-1.2.6 – Please provide a citation.

Response: We added a citation that has a detailed description of the ESR procedure: *J. Mater. Chem. A* **4** (15), 5448-5456.

-1.3.3 – How is this measured? Please describe the actions/equipment necessary.

Response: We added the detailed procedure for this measurement, which is copied below for easy review.

"1.4.3) 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. The area-specific resistivity (ASR) was calculated through multiplying the ohmic resistance (high-frequency impedance) by the active area of the flow cell."

-1.3.4 – How is this performed? Is this manually adjusted or via software?

Response: We added the detailed procedure for this operation, which is copied below for easy review.

"1.4.4) 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."

-Equipment should also be listed in the materials table (ie spectrophotometers, etc.).
Response: We added the information of the equipment used in this study to the Materials Table, including the battery tester, the electrochemical workstation, and the glove box.

4. Please remove all commercial branding: Line 133 - MBraun

Response: We replaced "a MBraun glove box" with "an argon-filled glove box".

5. Please obtain explicit copyright permission to reuse any figures from a previous publication. Explicit permission can be expressed in the form of a letter from the editor or a link to the editorial policy that allows re-prints. Please upload this information as a .doc or .docx file to your Editorial Manager account. The Figure must be cited appropriately in the Figure Legend, i.e. "This figure has been modified from [citation]."

Response: This research was originally published in Journal of Materials Chemistry A. According to their policy, the authors can reuse the published figures without obtaining permission, but they do require adding a sentence of "**The authors also acknowledge**

Also, we added "**This figure has been modified from Ref. 25.**" at the end of the caption for each figure.

2. Answers to the questions and comments from Reviewer #1

Manuscript Summary:
The article provide a clear description of a method that could be used to determine the concentration of a redox chemistry systems that can be used as a diagnostic tool to evaluate the state of charge of a flow battery during operation. This study is of great scientific and technological interest to the field of flow battery for energy storage applications.

Response: We thank the reviewer for the positive comments.

Major Concerns:
-Lines 187 - 189:
Step 1.3.3), The authors mention that measurements of the area-specific resistivity of the flow cell were performed by using EIS. However, they are not reporting nor discussing the result in the manuscript. Is this a representative result or why is this step described in the protocol? The reviewer suggests to include a short sentence in the results section to report this value. The measured area-specific resistivity value could help to briefly explain some ohmic losses in the system, thus, the low voltaic efficiency reported by the authors.

Response: We thank the reviewer for this careful reviewing. We added the ASR information in the section of Representative Results, which is copied here for easy review.

"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 1d). The low VE was registered by the relatively high cell ASR of 21.2 Ω cm^2 that was closely associated with limited ionic conductivity at such a high electrolyte concentration."

-Line 258: The reviewer suggests to include a short sentence to report the area-specific resistivity of the flow cell here, after (Figure 1d). For example " The low VE reported may be associated to some ohmic losses related to a poor electric contact of the cell parts or low ionic conductivity of the electrolyte as register by the area-specific resistivity of the cell".

Response: This comment is about the same concern as the immediately previous one. We've added the ASR information in the section of Representative Results, which is copied here for easy review.

"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 1d). The low VE was registered by the relatively high cell ASR of 21.2 Ω cm^2 that was closely associated with limited ionic conductivity at such a high electrolyte concentration."

-Lines 315-320. Did the author register the OCV of the flow cell while taking the sample during the charging stages? Does the estimation of the SOC by considering the OCV of the flow cell correspond to that SOC estimated by FTIR and ESR? How do they compare? The OCV also relates the ratio in concentration of the charged to discharged species in the system. It may be also demonstrative and helpful that the authors report the SOC by OCV analysis in Figure 3d.

Response: We thank the reviewer for this in-depth comment. We strongly agree with the reviewer that the OCV can be potentially used to determine the SOC of flow cells. This idea has been precedented for aqueous vanadium flow batteries in a published journal article (Tang et al, ECS Transactions, 2012, 41, 1-9), but a 5~7% deviation from Nernst Equation was indeed observed. Unfortunately, we didn't record the OCV of the PTIO flow cell when measuring the SOC using FTIR. But the ESR has been demonstrated as a good technique candidate to cross-validate the FTIR results.

Minor Concerns:
-Please attend suggestions in quotation marks or include additional information/description in some protocol steps.

Response: We thank the reviewer for this comment. We incorporated these suggestions in the revised manuscript.

-Lines 144 -145: 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.

Response: The phrases in these quotation marks were added.

-Lines 164 -165: Fully charge the flow cell at a constant current "density" of 5 mA/cm2 Stop the charging and the In step 1.2.4, did the author use a battery tester or a potentiostat /galvanostat equipment to perform charging/discharging experiments of the flow cells at constant current density? Please include this information. pump.

Response: The "density" was added. The battery tester was added.

-Lines 218 - 219: Please refer to Table 1. Add the units of weight (g) for each of the chemical compound names provided in Table 1.

Response: The units of weight for each compound were added in Table 1.

-Line 265: The reviewer recommends to cite previous published literature to refer the FTIR analysis of the N-O bond. It may be some research or at least a FTIR handbook.

Response: The citation of SDBS (Spectral Database for Organic Compounds) was added, which is copied below for easy review.

"(31)   SDBS, http://sdbs.db.go.jp, accessed on January 7, 2016."

-Line 279: There is a typo. It should be "Equation 1".

Response: This typo was corrected.

-Table of materials/equipment. The reviewer recommends to include in the table the name/company of the electrochemical workstation that was used to perform the electrochemical or/and the EIS tests. Additionally, the reviewer recommends to include the name/company of the battery tester, if so, that was used to carry out the flow battery test.

Response: The detailed information of the battery tester and electrochemical workstation was added in the Materials table.

Additional Comments to Authors: N/A

3. Answers to the questions and comments from Reviewer #2

Manuscript Summary:
The authors present a protocol for the full electrochemical and spectroscopic analyses required to monitor the state of charge of a flow battery electrolyte employing an IR-active charge-storing species. This is a new state of charge monitoring technique, and, given its direct application to nonaqueous flow batteries, is a difficult technique to perform. Thus, this protocol is likely to be useful for the research community and I would recommend this article for publication in JoVE, pending the improvement of detail in the protocol and adjustments to points in the main text:

Response: We thank the reviewer for the positive comments.

1. The authors propose electrolyte volumes and cycling conditions unique to their flow cell design. The flow cell design itself, is not available to the reader. Either the flow cell design should be available to ensure the experiments can be reproduced identically, or the authors should adjust the protocol to teach readers how to perform the same experiments on their own flow cell hardware.

Response: We thank the reviewer for this comment. We added the photographs of our flow cell design as a new Figure 1, which is copied here for easy review.
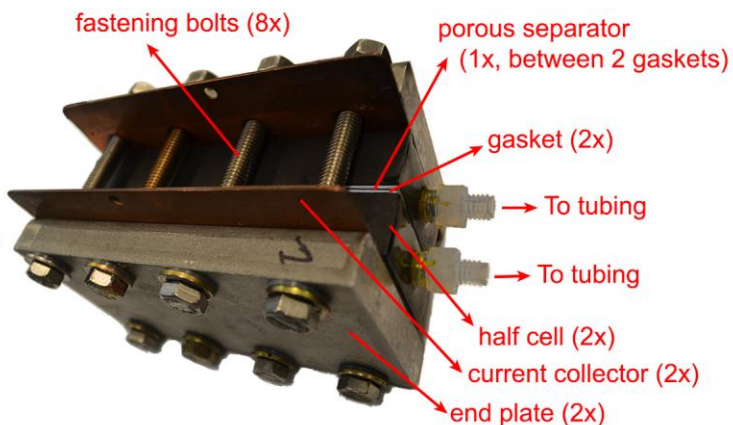
"

Figure 1: The photograph of the flow cell assembly
"

2. Throughout the protocol, the authors list masses of chemicals to add to their electrolyte solutions. Please also add values for the final effective concentrations of active species, as the final concentrations are important for proper interpretation of the electrochemical data. Approximate final electrolyte volumes should also be listed.

Response: We thank the reviewer for this comment. The molar concentrations were added throughout the protocol, wherever the electrolytes were prepared using masses of chemicals.

3. An additional benefit of FTIR over UV-vis is that the FTIR method cannot saturate its detector. The FTIR method thus can rely on versatile spectroscopic equipment than the more well established UV-vis technique.

Response: We thank the reviewer for this valuable information. We added this advantage of FTIR to our manuscript, which is copied here for easy review.

"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."

4. The protocol for a CV experiment is listed, but the introduction does not mention anything about CV. Please add some discussion as to the relevance of the CV technique to monitoring state of charge. Note that, iIn my opinion, the CV is not necessary to measure SOC.

Response: We thank the reviewer for this question. The purpose of the CV is simply to determine the redox potentials of the PTIO redox couples, which could help define the voltage cutoff limits in PTIO flow cell tests. And we also observed excellent stability of the redox couples under CV conditions. We agree that CV is not necessary to SOC measurements at all.

5. Instead of using a Ag/Ag+ quasi-reference electrode, which is known to have an unstable potential drift over time, the authors should consider using the silver-cryptand reference electrode instead: A. Lewandowski, M. Osińska, A. Swiderska-Mocek, M. Galinski, A Cryptate Reference Electrode for Ionic Liquids, Electroanalysis. 20 (2008) 1903-1908. doi:10.1002/elan.200804267.

Response: We thank the reviewer for this valuable information. We did observe the potential drift for Ag/Ag+ electrode. We'll try the silver cryptand reference electrode in future studies. We have also added the following text to acknowledge the quasi-reference nature of our reference electrode:
"1.1.5) … It should be noted that our 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."

6. Lines 67-68: Why does a symmetric RFB lead to high solubility? Just because the active species is ambipolar does not imply anything about its solubility.

Response: We thank the reviewer for this question. To clarify, a symmetric RFB design can help increase the effective redox concentration, not the actual solubility. To overcome the materials crossover issue, mixed-reactant electrolytes that contain both anolyte and catholyte electroactive materials (at 1:1 ratio) were used to reduce the concentration gradient. This strategy is effective in achieving low capacity fading, but greatly sacrifices the effective redox concentration, even though the actual solubility may be high. Typical such examples include iron/chromium and iron/vanadium flow batteries.

7. Lines 114-115: Please add that electrolyte conductivity measurements is another method that has been explored for SOC monitoring.

Response: We added this method for SOC monitoring in the revised manuscript, which is copied here for easy review.

"However, this area seems to be under-addressed so far, especially in nonaqueous 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.[22-24]"

8. Line 120: MeCN is not a typical battery solvent. No widely used battery technologies use MeCN as an electrolyte solvent.

Response: We agree that MeCN is not a typical solvent for batteries. In our flow battery environment, MeCN has high ionic conductivity (with supporting salt), low viscosity, and electrochemically stable voltage window for the PTIO flow chemistry. This is particularly attractive for nonaqueous flow batteries to deliver good cell efficiencies, high material utilization, and decent cyclability.

9. Line 144: Is the graphite felt counter electrode dried before use?

Response: Yes, we need to dry the graphite felt counter electrode to remove moisture.

10. Lines 144-145: AgNO3 typically exhibits very low solubility in most solvents. When using a Ag/Ag+ non-aqueous reference electrode, it is typical to add a supporting electrolyte, such as TEABF4. As an alternative to AgNO3, AgBF4 has a much higher solubility in MeCN, and is sufficiently conductive to provide a good quasi-reference electrode.

Response: We thank the reviewer for this valuable information. AgNO3 indeed has low solubility in most organic solvents. AgBF4 is a good alternative to AgNO3. We also used AgOTf (silver triflate) in the reference electrode, which has high solubility in most organic solvents.

11. Line 154: What type of porous separator is used?

Response: The porous separator is polyethylene/silica composite separator obtained from Daramic, LLC. This information was already in the Materials Table.

12. Lines 160-162: The 4 mL volume of electrolyte is extremely small, especially considering the 10 cm^2 cell active area. How do the authors ensure that the cell is always filled with electrolyte and that gas bubbles are not introduced?

Response: We used thin graphite felts (3mm thickness) and thin tubings (1/16" ID). These ensure low volume (~3mL) of electrolytes filling the cell parts, and the rest volume (~1mL) remaining in the glass vial.

13. Line 206: Why does the spectroscopy cell need to be mounted quickly?

Response: The nonaqueous flow battery samples are potentially air-sensitive. Although the FTIR cell was already sealed tightly to avoid air, we were trying to minimize every possibility of air contact with the sample.

Major Concerns: N/A
Minor Concerns: N/A
Additional Comments to Authors: N/A