**Response to Reviewers and Editorial Comments on**

**“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.

“



**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 cm2 using a razor blade. Similarly, cut a porous separator to an area of 3 x 12 cm2.”

-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/cm2 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 Journal of Materials Chemistry A (a Royal Society of Chemistry journal) for originally publishing this research (**[**http://pubs.rsc.org/en/content/articlehtml/2016/ta/c6ta01177b**](http://pubs.rsc.org/en/content/articlehtml/2016/ta/c6ta01177b)**)**” to the Acknowledgement. We have fulfilled this request.

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 cm2 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 cm2 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

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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