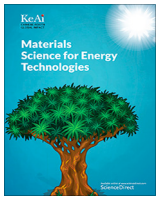
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# Understanding degradation of electroactive molecules in organic redox flow batteries: Decomposition analysis methods



Sikukuu khwa Museveni [a], Godfrey Nakitare Nambafu [a], Naomi Kollongei [b,*]

[a] Turkana Technical College, Lodwar, Kenya
[b] KCA University, Nairobi, Kenya

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ABSTRACT

Organic redox flow batteries have attracted a lot of interests both in academics and industries. Accordingly, many organic materials and chemistries have been studied, providing a solid foundation for development of low-cost organic flow batteries. However, capacity loss/fade as a result of organic molecule decomposition/degradation is a major hindrance towards further advancement of this promising, sustainable and large-scale energy storage technology. Understanding the causes of decomposition as well as its mechanism is thus necessary to unravel this major challenge. Therefore, this perspective/views focus on highlighting the different methods that can be employed for decomposition assessment of organic molecules in flow battery systems. This will help in engineering and designing stable electroactive organic molecule to enable development of durable and long cycle life redox flow battery.
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## 1. Introduction

Organic materials have become progressively attractive for application as electroactive materials in redox flow batteries (RFBs). This is due to their unique properties such as nature/earth abundant, environment-friendly, and synthetic tailorability [1]. In the last few years, there have been introduction of various new and modified organic redox active materials/couples for application in organic redox flow batteries (ORFBs). The preferred ideal properties of suitable organic redox active materials are high solubility, high cell voltages, faster electrochemical kinetics, and exceptional good stability [1-4].

Despite the various merits, further development and advancement of organic redox flow batteries have been hindered by many challenges such as low energy density, low cycle life, low efficiency, membrane issues etc. Generally, low cycle life as a result of capacity loss/fade during cycling is one of the major challenges encountered [4-7]. There are many factors that lead to capacity loss in ORFBs, namely crossover issues, electrode passivation, self-discharge, molecule decomposition, side reactions etc. However, research has shown that molecule self-degradation or electrolyte side reactions are the major causes of capacity loss in ORFBs. Therefore, there is need to address this challenge [8,9].

Solving this problem requires a deep understanding of the decomposition mechanism of the organic materials. Understanding the decomposition pathway and causes of decomposition will be key towards addressing this challenge. As well, this will be crucial towards synthetic tuning and engineering of stable and suitable organic redox active molecules. Addressing this challenge necessitates the development of durable and long cycle life ORFBs [8-10].

A few articles have employed some methods to study the decomposition of the redox active materials during cycling in ORFBs. This is due to the fact that, decomposition analysis during cycling is essential in understanding capacity fade issues in the battery [11-15]. Moreover, to solve these degradation issues, it will be highly important to report the resulting products after decomposition and propose decomposition pathways/mechanisms for these molecules. Therefore, to make this possible, there is need to consider and apply different techniques. In this work, we highlight the various methods used in investigating decomposition of organic molecules. Also, the current advances, and future perspectives are discussed.

## 2. Decomposition assessment methods

Organic electroactive materials can be studied using various techniques i.e., spectroscopies as well as computational simulations as shown in Fig. 1 [16-19]. Availability of different analysis techniques is one of the many reasons that has propelled massive

* Corresponding author.
*E-mail address:* kolongei@kcau.ac.ke (N. Kollongei).

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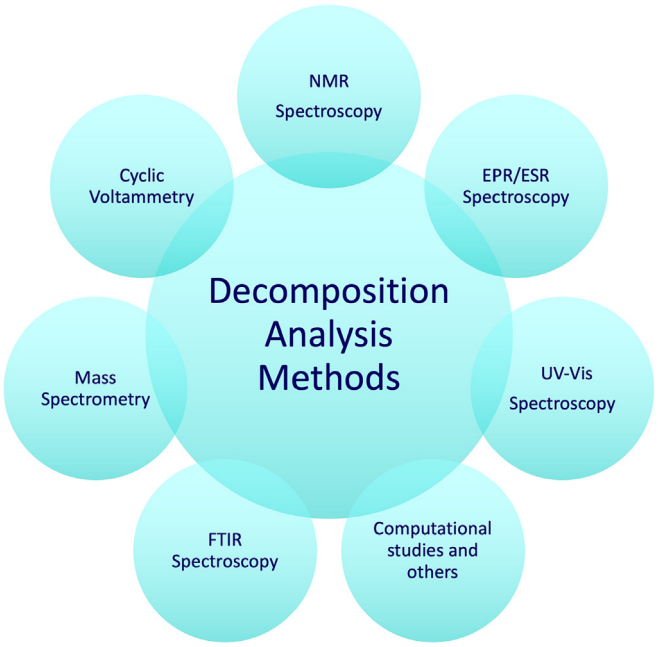



**Fig. 1.** The schematic of the different characterisation and decomposition assessment approaches applied in organic redox flow batteries.

research works and interests in this ORFBs. Various excellent works have employed the various techniques in characterisation of organic molecule and also in molecule degradation assessment studies. This work summarises the main techniques that can be used in analysis of organic molecules.

## 3. Cyclic voltametric study

Cyclic voltammetry (CV) is an important electrochemical technique used to study redox processes of analytes/molecules [20]. In RFBs, it's used to identity redox couples and redox potentials of the redox active molecules, among many other uses [21,22]. This technique is used to study decomposition by comparing the CV curves of fresh electrolyte with that of spent electrolyte [23,24]. Disappearance or size reduction of the original redox peaks and appearance of new peaks are some of the indicators of possible decomposition. Also, changes in peak current and potential can be crucial in evaluating decomposition of the molecules. Daniela Pinheiro and colleagues used CV measurements to study the stability of electrolytes in a sulfonated tryptanthrin based RFBs. Cyclic voltammogram profiles of sulfonated tryptanthrin (TRYP-$SO_3H$) and 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt monohydrate (BQDS) indicated degradation of the active materials. There were emergence of new anodic and cathodic peaks in the cycled TRYP-$SO_3H$. Also, CV results of TRYP-$SO_3H$ displayed higher current density in the redox peaks of the fresh electrolyte in comparison to cycled electrolyte. Theseindicate potential loss of the active material. CV measurements of BQDS exhibited a new peak which was associated with degradation as a result of Michael addition reaction [25]. CV measurements were also used by Fahad Alkhayri et al. to study the stability of bispyridinylidene anolytes and TEMPO catholyte for non-aqueous redox flow batteries (NARFBs). Cyclic voltammograms indicated crossovers of both anolyte and catholyte across the anion exchange membrane. Also, CV confirmed decomposition of the catholyte, with presence of new peaks at 0.0 V and −0.7 V confirmed presence of new species [26]. Fig. 2 demonstrates application of CV studies in examining degradation of electrolytes in RFBs.

## 4. Mass spectrometry

Mass spectrometry (MS) is an analytical technique that measures the mass-to-charge ratio ($m/z$) to quantify and identify molecules [27-29]. The different kinds of MS such as Liquid Chromatography-Mass Spectrometry (LC-MS), Matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF), Inductively coupled plasma mass spectrometry (ICP-MS), Direct Analysis in Real Time Mass Spectrometry (DART-MS), Secondary ion mass spectrometry (SIMS), etc can all be employed to study organic electro active molecules [30,31]. Changes in the peaks are key indicators of possible degradation or modification of the molecules (Fig. 3). Xu Donghan et al. used Gas Chromatography-Mass Spectrometry (GC–MS) to study decomposition in NARFB based on 2,5-di-*tert*-butyl-1-methoxy-4-[2′-methoxyethoxy] and 3-nitrotoluene (3-NT) as catholyte and anolyte respectively. Mass spectra data showed emergence of new peaks confirming degradation of 3-NT to form 3,3′-dimethylazobenzene during battery cycling [32]. LC-MS was also employed by Bo Hu and his colleagues to study the stability of electrolytes in 3-carbamoyl-2,2,5,5-tetra methylpyrroline-1-oxyl (CPL) based neutral aqueous RFB. The mass spectrum of the cycled CPL electrolyte displayed an extra peak at mass to charge ratio of 151.89 which corresponded to positive-charged diene structure. This was associated with CPL undergoing a ring-opening side reaction on the nitroxide radicals caused by attacks of water [33].

## 5. Nuclear magnetic resonance (NMR) spectroscopy

This technique allows analysis of molecular structure of organic molecules through measuring and observing interactions of nuclear spins with radiofrequency electromagnetic radiations in a strong magnetic field [34-36]. Wang Caixing et al. used NMR to study the stability of 2,6-diaminoanthraquinone, namely, N, N'-(9,10-anthraquinone- 2,6-diyl)-di-$\beta$-alanine (DAEAQ) anolyte in an aqueous RFBs. NMR spectrum of cycled DAEAQ anolyte showed new peaks confirming irreversible degradation of the molecule which was the main cause of capacity fade in this battery chemistry. In control experiments, H NMR spectrum confirmed presence of by products by presence of new peaks, when the DAEAQ anolyte was stored at 80 °C for 7 days [37]. H-NMR analysis were also used to confirm degradation of 3,3′-dimethylaminemethylene-4,4′-bip henol (DABP) catholyte in silicotungstic acid (SWO)/DABP flow battery as reported by Liu Wanqiu et al. The decomposition was reported to be caused by side reactions of DABP with solvent molecules which was confirmed by new peaks in the NMR spectrum [38]. NMR can play an important role in decomposition studies of electroactive materials in RFB as shown in Fig. 4.

## 6. Fourier-transform infrared (FTIR) spectroscopy

Fourier-transform infrared (FTIR) spectroscopy is an analytical technique that is used to identify organic molecules. An infrared absorption spectrum is produced, identifying the chemical bonds and functional groups present in the molecule [39,40]. Disappearance of peaks or/and emergence of new peaks signifies formation of new functional group(s) [41]. The changes in the spectra indicate possible decay or decomposition of the redox active materials as shown in Fig. 5. Duan, Wentao, et al. demonstrated the use FTIR in evaluating the concentration of electrolytes and state of charge of the 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (PTIO) based symmetric flow battery. FTIR study was able to distinguish the three PTIO species i.e. PTIO, $PTIO^+$ and $PTIO^-$ and their concentration during the charge/discharge process, making it easier to detect any change in the active molecule [42]. Liang,

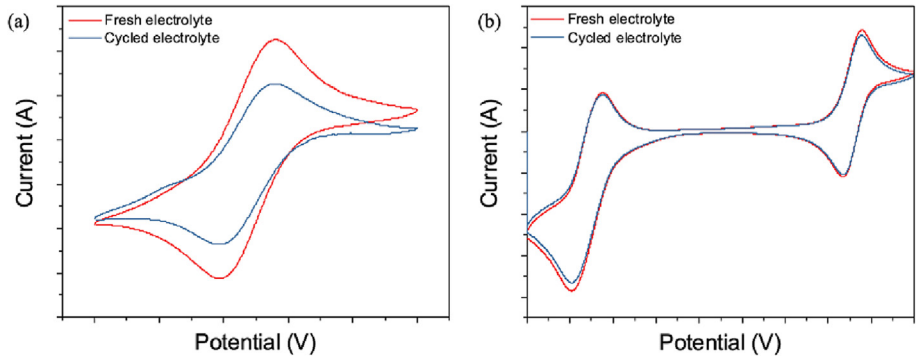



**Fig. 2.** Schematic illustration of cyclic voltammograms of fresh and cycled electrolytes (a) one redox couple, (b) two redox couples.

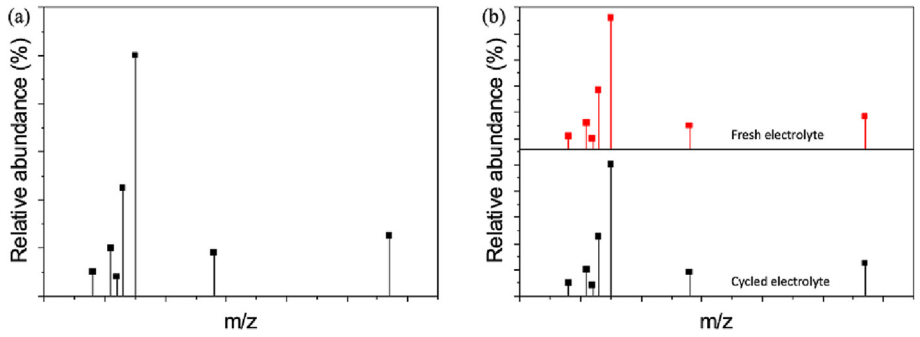



**Fig. 3.** (a) Schematic illustration of mass spectra of (a) characterisation of redox active material (b) comparison of fresh and cycled electrolytes.

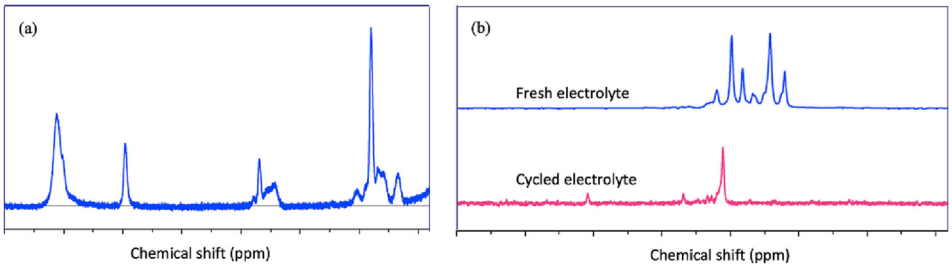



**Fig. 4.** Schematic NMR spectra showing (a) representative spectrum of a redox active molecule, (b) comparison of fresh and cycled electrolytes.

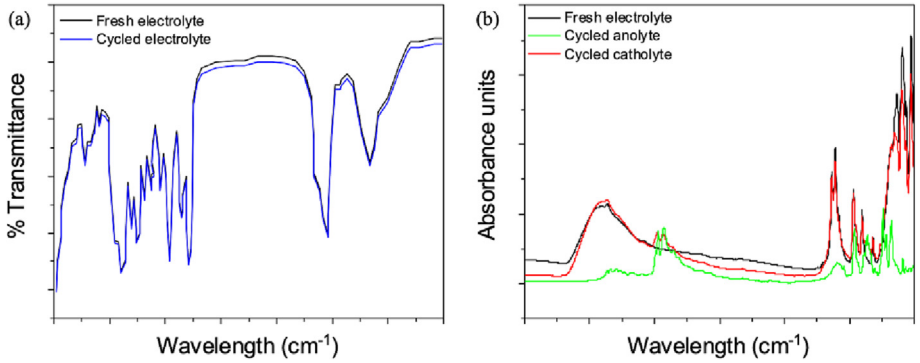



**Fig. 5.** Schematic illustration of utilising FTIR spectroscopy in decomposition study of redox active materials (a) plot of transmittance vs wavelength, (b) plot of absorbance vs wavelength.

Zhiming and colleagues also employed attenuated total reflectance-fourier-transform infrared (ATR-FTIR) to study the stability of active materials in a NARFB utilising viologen-based polypeptide as negative material and TEMPO-based polypeptide as positive electroactive material. ATR-FTIR spectra of the electrolytes confirmed α-helical backbones remained unchanged, by

presence of signatures at 1650 and 1550 cm $^{-1}$, before and after cycling. Also, the esters' linkages between the redox active groups and the backbones were confirmed to be unchanged by ATR-FTIR signature at 1730 cm$^{-1}$. These indicated good stability of these groups [43]. These works confirm FTIR spectroscopy can be an ideal technique in decomposition studies in RFBs.

## 7. Ultraviolet–visible (UV–Vis) spectroscopy/spectrophotometry

Ultraviolet–visible (UV–Vis) spectroscopy analyses a molecule sample/ analyte sample by measuring the intensity of light absorbed/-transmitted in the part of the ultraviolet and visible regions of the electromagnetic spectrum. Absorbance and transmittance are usually influenced by sample composition and concentration thus enabling analysation and quantification of molecules [44,45]. In this technique, loss of peak intensity or formation of new peak is an indication of possible decomposition of the redox active materials (Fig. 6). Liu Lei et al. used UV–Vis spectroscopy to study the stability of ethyl viologen radical with or without α-cyclodextrin (α-CD) as a spectator in organic aqueous RFB. UV–Vis results of EV radical cation (EV•+) without α-CD revealed decomposition over nine days examination period. On the other hand, UV–Vis result of the cation with α-CD spectator showed better stability as very minimal decay was observed. They confirmed the ability of α-CD to stabilize the EV radical through suppressing of viologen radicals dimerization reactions [46]. Kwon, Giyun and co-workers investigated 5,10-dihydro-5,10-dimethyl phenazine [DMPZ]) as a positive redox active material in RFB. They also utilized UV–Vis spectroscopy to examine the stability of intermediate radical cations during the redox process of DMPZ. UV–Vis spectra of DMPZ$^{+}$ remained unchanged during 24 hrs observation period, confirming the good stability of the intermediate radical cation [47]. Attanayake, N. Harsha, et al. employed UV–Vis spectroscopy to investigate the stability of organic radical cations, as posolytes in non-aqueous RFBs. The study showed that positive redox active materials with low oxidation potentials have better stability than the higher oxidation potential catholytes. N-Ethyl-3,7-dimethoxyphenothiazine tetrafluoroborate (DMeOEPT-BF4), N-ethyl-3,7-dimethylphenothiazine tetrafluoroborate (DMeEPT-BF4), 4,4,4-trimethoxytriphenylamine tetrafluoroborate [(MeOPh)3N-BF4], N-ethylphenothiazine tetrafluoroborate (EPT-BF4), and N-((2-methoxy)ethoxy)-ethylphenothiazine tetrafluoroborate (MEEPT-BF4), are the low to moderate oxidation potential positive materials that were investigated. On the other hand, N-Ethyl-3,6-dimethoxycarbazole tetrafluoroborate (DMeOECz-BF4), N-ethyl-3,7-bis(trifluoromethyl) phenothiazine tetrafluoroborate (BCF3EPT-BF4), 1,4-Di-*tert*-butyl-2,5-dimethoxybenzene tetrafluoroborate (DDB-BF4), and (N-Butylethylamino) cyclopropenium bis-tetrafluoroborate [BECP-(BF4 )$_2$], are the higher oxidation materials that were examined [48].

## 8. Electron paramagnetic resonance (EPR) or electron spin resonance (ESR) spectroscopy

Electron paramagnetic resonance (EPR) spectroscopy is an analytical technique used to study materials with unpaired electrons such as transition metal ions and free radicals [49,50]. This is an important tool in studying organic radicals which are also applied as redox active molecules in ORFBs as shown in Fig. 7. Zhao, Evan Wenbo, et al. used EPR to study 2,6-dihydroxyanthraquinone (DHAQ) as an electroactive material in aqueous RFB. EPR revealed that DHAQ undergo two subsequent one electron transfer redox process (DHAQ$^{2-}$→ DHAQ$^{3-\bullet}$ and DHAQ$^{3-\bullet}$ → DHAQ$^{4-\bullet}$). In addition, EPR showed a competing dimerization reaction involving two of the unpaired electrons of the radical anion (DHAQ$^{3-\bullet}$) leading to an EPR-silent anion [51]. This work confirms EPR can play a useful role in decomposition analysis of active materials in redox flow batteries. Also, Huang, Jinhua and co-workers employed EPR to investigate 1,4-dimethoxybenzene derivatives in RFBs. EPR was used to study the structure and stability of various radical cations. The study revealed decomposition/decay of the radical cations and they proposed a potential reaction pathway for the cation decay i.e., radical addition, radical disproportionation and deprotonation followed by hydrogen atom abstraction from the solvent to form a neutral molecule. Ideally, radical addition and radical disproportionation can lead to active material loss hence capacity decay in RFBs [52]. Sevov, Christo S et al. used EPR spectroscopy to study a benzoylpyridinium-based anolyte RFB. EPR helped them establish the ideal electrolyte pH for achieving good stability and long-term cycling. In addition, they revealed decay of the molecule at low pH and provided insights of the decomposition pathway of this negative redox active material [53].

## 9. Computational studies

Computational study has proven to be a useful tool towards advancement of organic flow batteries. Much work have been done on functionalisation and design of organic materials to enable them attain suitable properties for an ideal electroactive material. However, to the best of our knowledge their exist no study focusing on understanding decomposition of these molecules under different cycling conditions. It's therefore necessary for researchers to focus on this. Combining experimental work and computational studies (as demonstrated in Fig. 8) will be critical towards efficient and quick diagnosis of these major issues. Liu Wanqiu et al. used

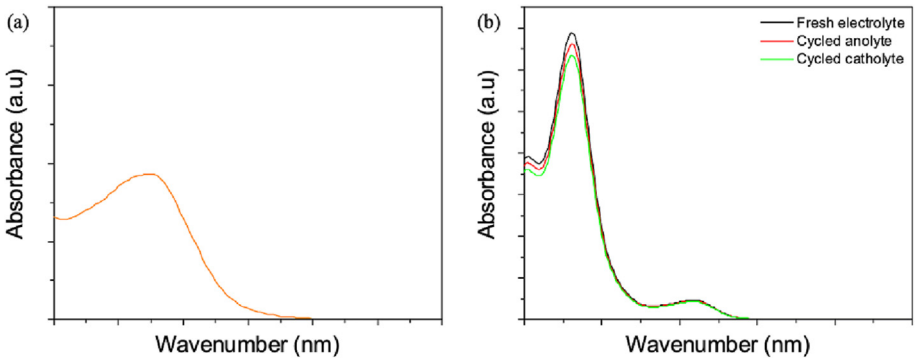



**Fig. 6.** UV–Vis spectra exhibiting (a) schematic characterisation of an electrolyte (b) comparison of fresh and cycled electrolytes.

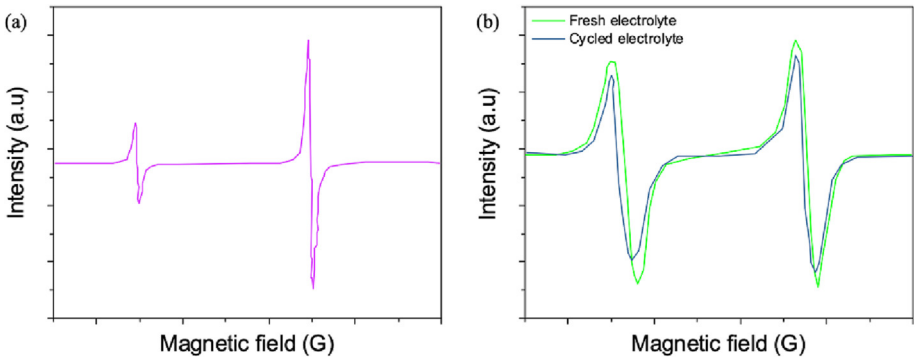



**Fig. 7.** Schematic EPR spectrum/spectra of (a) schematic characterisation of a redox active material (b) comparison of fresh and cycled electrolytes.




**Fig. 8.** Schematic computational simulation showing decomposition of redox active material.

DFT studies to confirm stability of biphenol molecules in aqueous RFBs. Computational studies confirmed (3,3′,5,5′-tetramethylami nemethylene-4,4′-biphenol (TABP) to be more stable than 3,3′-di methylaminemethylene-4,4′-biphenol (DABP). DFT calculations confirmed differences in average ß-C charge and the molecular electrostatic potential (ESP) between the two molecules. TABP was observed to have a more negative ESP around ß-C atoms making it less susceptible to attacks by solvent molecules. In addition, TABP was observed to be stable and air insensitive because of the presence of ammonium functional groups making it less susceptible to Michael addition reactions [38].

## 10. Summary and outlook

This work highlights the major analytical techniques and their application in studying the decomposition of redox active materials in RFBs. It's important to note that these are not the only techniques that can be employed. Other techniques such as Raman spectroscopy, among many others not mentioned here can also be employed to perform the discussed roles. The main purpose of this work is to echo how important it is to investigate the decomposition of active materials in redox flow batteries. Notably, identifying the causes of degradation, the decomposition mechanisms and the decomposition products are crucial. These will provide key insights to facilitate molecular engineering of highly stable redox active organic materials for application in large scale and long cycle life redox flow batteries.

Most studies have employed ex situ analytical techniques in decomposition assessments and have shown promising results. Recently, in operando and in situ redox active material characterization in flow batteries are becoming a successful. These tools are equally important in unravelling the decomposition causes, mechanisms and products of electroactive materials in RFBs. However, in situ and in operando techniques are more ideal as they provide real-time results and enable continuous monitoring and analysis of the redox active materials during the RFB's charge and discharge processes. Most of the characterization tools provide structural information of redox active molecules. However, in selecting the ideal techniques for decomposition assessment in RFBs, features such as accessibility, cost, compatibility with RFB system for easy incorporation, response time etc. should be considered. In addition, these tools should be able to distinguish between the solvent, supporting ion and the electroactive materials, differentiate the active materials at different redox state, differentiate the active materials from the side reaction/decay products and determine the concentration or change in concentration of the electrolytes [42].

As demonstrated above, these techniques have the capacity to provide detailed study of the decomposition pathways of active materials in RFBs. The techniques can be applied solely or combined (various techniques utilized together) to achieve better understanding of the structural modification of redox active materials. Combining experimental and computational research efforts will also be critical in providing essential data for development of ideal redox active materials for long cycle life RFBs.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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