Characteristics of all organic redox flow battery (AORFB) active species TEMPO-methyl viologen at different electrolyte solution

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Abstract. The practice of using wind and solar energy to generate electricity represents a solution that would be beneficial for the environment and ought to be explored. However, in order to ensure users' stability and continuous access to electricity, the increasing usage of renewable energy needs to align with the advancement of energy storage technologies. Redox flow batteries, which use organic solution as the electrolyte and a proton exchange membrane as an ion exchange layer, are currently the subject of extensive research as one of the alternative renewable energy storage systems with the benefit of a techno economy. This study investigated the solubility of organic solution, namely 2,2,6,6-Tetramethylpiperidinylxox or 2,2,6,6-Tetramethylpiperidine 1-oxyl (TEMPO) and methyl viologen (MV) in various essential electrolyte solutions such as NaCl, KCl, KOH, and H\textsubscript{2}SO\textsubscript{4} that can be used as electrolytes of all organic redox flow battery (AORFB) system to produce high energy density and charging and discharging capacity. The result shows the optimum condition for effective charge transfer in AORFB is TEMPO catholyte and MV anolytes at the 0.08 M H\textsubscript{2}SO\textsubscript{4} electrolyte solution. Additionally, a correlation between the acquisition of electrolyte solutions on TEMPO catalyst and MV anolytes was discovered by the data. Electrolyte solution can improve electrical conductivity in TEMPO solution, which in turn can improve the efficiency of AORFB charging and discharging. Contrarily, MV anolytes exhibit a different pattern where the addition of electrolyte solutions reduces their electrical conductivity. RFBs systems with the aforementioned catholyte and anolyte can be used to store solar energy with a maximum current of 0.6 A for 35 minutes. Storage effectiveness is characterized by a change in colour in the catholyte and anolyte. The findings firming the possibility of using AORFB as one of the alternative energy storage systems that can accommodate the intermittence of the renewable energy input resource.

Keywords: redox flow battery, anolyte, catholyte, methyl viologen, TEMPO

1. Introduction

Energy supply stability and capacity are critical to the long-term development of society since they are both the foundation for human existence and the source of power for societal advancement. Enhancements to energy supply capacity and security face significant challenges because the current fossil fuel-based energy infrastructure cannot meet the demands of sustainable societal growth. Consequently, research into clean and effective renewable energy is required (Kim et al., 2011; H. Zhang et al., 2019). Although renewable energy sources like solar and wind can produce electricity, natural factors like seasonal variations and day-night cycles greatly affect their availability (Chamundeswari et al., 2021; Soloveichik, 2015; Strielkowski et al., 2021; Zsiborács et al., 2019). Frequently, the electricity produced is unpredictable, erratic, and sporadic (Díaz-González et al., 2012; Kim et al., 2011; H. Zhang et al., 2019). Technology for energy storage is required to address this problem. According to (Dunn et al., 2011; Leadbetter & Swan, 2012; Yuan et al., 2018), it may stabilize power output, regulate power generation, and provide amplitude modulation and frequency regulation. These features enable electricity continuity, stability, and controllability.

The relationship between intermittent renewable power sources and energy demands is crucially dependent on energy storage (H. Chen et al., 2018; Singer & Peterson, 2011; Zanzola et al., 2017). To successfully use renewable energy sources and create a sustainable society, advanced large-scale energy storage technologies are essential. Flow batteries have been recognized as a promising technology for large-scale energy storage among other energy storage devices (Alotto et al., 2012; S. Liu et al., 2020; Pan et al., 2023; Yuan et al., 2018).

One or more electroactive species dissolved in a liquid electrolyte store energy in a rechargeable flow battery (Zhen & Li, 2019). In order to directly transform chemical energy into...
electrical energy and vice versa, electrolytes are kept apart in a box outside of their electrochemical cells and pumped through electrochemical compartments (Asenjo-Pascual et al., 2022). While energy density or output is dependent on the size of the tank, power density is determined by the design and size of electrochemical cells (Y. Liu et al., 2021). These qualities enable flow batteries to be used for an extended period of time in a variety of static energy storage systems (Badwal et al., 2014; H. Chen et al., 2018; Joseph et al., 2022; Nguyen & Savinell, 2010).

According to various studies (Chai et al., 2020; Soloveichik, 2015), flow batteries are highly efficient (Likit-Anurak et al., 2017; Wu et al., 2014), and they are inexpensive. They can also be utilized extensively (Aren & Walsh, 2022; Lim et al., 2015). The system’s scalability and adaptability allow the flow battery to effortlessly achieve the kW to MW range (Arabkoohsar, 2021). It promotes the development of flow batteries, which are presently concentrated on energy storage in networks in conjunction with renewable energy generation, or power systems in isolated, stand-alone locations (Arnberg et al., 2019; Park et al., 2019).

Two liquid electrolytes with dissolved metal ions are pumped in the direction of electrochemical cells in the redox flow battery (RFB). Catholyte and anolyte are the terms used to describe the electrolytes in negative and positive electrodes. During charging and discharging, metal ions stay dissolved in the electrolyte fluid and do not undergo any phase shifts. Membranes that permit positive ions to cross for electron transfer activity separate the anolyte and catholyte. Batteries-powered devices can exploit the current that runs over the electrodes during charge exchange. The dissolved active mass of the tank is constantly fed to the electrodes during charge exchange; the converted product is then returned to the tank (Arabkoohsar, 2021; Badwal et al., 2014; R. Chen et al., 2017; Zhen & Li, 2019). In Figure 1, the RFB flow system is displayed.

Initially, RFBs are not suitable for static rechargeable batteries due to its dissociated energy (the volume of the electrolyte reservoirs) and power (the electrode surface area). This is good for essential power-supplying operations, nevertheless. The distinct cell architecture is the cause of this characteristic. Second, due to its quick electrochemical kinetics and the high conductivities of the supporting electrolytes, RFBs can function at large currents (> 50 mA/cm²) and high-power densities (in the order of 102 mW/cm²). Third, the non-flammable aqueous electrolyte used in aqueous redox flow batteries (RFBs) makes them safe options for energy storage (B. Hu et al., 2018; Soloveichik, 2015; Wang et al., 2013; Z. Yang et al., 2011).

The performance of RFBs is defined by energy density and cycle stability (Yao et al., 2021; Zhou et al., 2023). Equation 1 below can calculate the number of charges stored and can be determined by calculating theoretical energy density. The ratio of average discharge and charging voltage at constant current, as well as the capacity of discharge and charging capacity (CE), determine EE. As an active pair of total reversible redox, high selectivity membranes can prevent cross-redox species, thereby protecting electrodes from corrosion. The durability of the RFB system is a representation of the stability of redox-active species, membrane separators, and electrodes (H. Chen et al., 2018; C. Zhang, Niu, et al., 2018).

First-generation RFBs, such as Zn-Br, and vanadium RFB, have developed into comparatively well-established technology. However, because of its high cost and restricted and caustic active components, its usage for large-scale energy storage is constrained by technological and economic limitations (B. Hu et al., 2017; Y. Liu et al., 2021). Recently, organic RFBs—a novel system—have been developed. Though it uses water-soluble organic molecules made of elements that are common on Earth, like carbon, hydrogen, oxygen, nitrogen, and sulphur, it functions on similar principles to vanadium RFB (Ding et al., 2018; Y. Liu et al., 2021; Pan et al., 2023; Wei et al., 2017; B. Yang et al., 2014; Zsiborás et al., 2019). It is economical and provides better safety. More crucially, organic molecules’ great diversity and ease of structural tailoring may result in qualities like water solubility, redox potential, kinetics, and stability that are needed for real-world applications (Kwabi et al., 2020; Y. Liu et al., 2021; Winsberg et al., 2017). Thus, organic RFB is viable for large-scale electrical energy storage (Zhou et al., 2023).

High power can be produced by the kinetics of organic chemical reactions occurring rapidly. It is possible to regulate the solubility of functional groups of active substances by utilizing the high solubility of organic molecules. Organic substances like quinone (Ding et al., 2016; Han et al., 2019; Jones et al., 2022; Wedege et al., 2016). Because the reactions are fast and inexpensive, TEMPO and viologen are feasible (T. Liu et al., 2016a). Research on RFBs with organic compounds is exciting to develop because the combination of these chemical compounds has not been extensively examined. When 9,10-anthraquinone-2,7-sulfonic acid (AQDS)-bromide was used as the electrolyte in RFBs systems, power densities of up to 1 W/cm² were obtained; these values were almost identical to those of 1.34 W/cm² vanadium RFBs systems (R. Chen et al., 2017).
2. Experimental method

2.1 Materials

TEMPO (2,2,6,6-Tetramethylpiperidin-1-oxyl) and Methyl Viologen (MV) were purchased from Shandong Zhi Shang Chemical Co., Ltd. The solvents—NaCl (Sodium chloride, ≥99.0%), KCl (Potassium chloride, ≥99.0%), KOH (Potassium hydroxide, ≥85%), and H₂SO₄ (Sulfuric acid, 99.0%)—were purchased from Sigma Aldrich. All the chemicals were used without prior pre-treatment.

2.2 Measurement of Solubility

In order to test the solubility of TEMPO and Methyl Viologen (MV) in different electrolyte solutions, the electrolyte solutions—NaCl, KCl, KOH, and H₂SO₄—are first prepared at a concentration of 1 M. Next, the electrolyte is added to the solution at concentrations of 0.02, 0.04, 0.06, 0.08, and 0.1 M. Based on the solution's absorption measurement on the UV-Vis Spectrophotometer, which reads 476 nm for TEMPO and 420 nm for Methyl Viologen, solubility is determined.

2.3 Implementation of the Active Species as AORFB for Solar Energy Storage System

After the solubility and conductivity test, the active species of MV and TEMPO in the electrolyte solution is implemented in AORFB for solar energy storage systems. The AORFB system is assembled as Figure 2. The system consists of an AORFB cell, anolyte and catholyte solution feeder with peristaltic pump, in connection with solar panel system. The AORFBs cell consist of sandwiched of aluminium plate 100 x 80 mm in sequence with current collector, carbon felt, silicone foam frame, proton exchange membrane (Commercial Nafion), silicone foam frame, Carbon felt, another current collector, and aluminium plate as shown in Figure 3.

3. Result and Discussions

3.1 Solubility of TEMPO Solution on various electrolyte solutions

An earlier work to build a totally organic aqueous redox flow battery served as model for the assessment of a water-soluble TEMPO derivative as a catholyte candidate. When used as the positive electrolyte in none-aqueous RFB, TEMPO exhibits reversible one-electron storage as well as a high redox potential in the organic solvent (S. Hu et al., 2021; Li et al., 2011; T. Liu et al., 2016a; Y. Liu et al., 2019). The molecule can be utilized in an aqueous redox flow battery attributed to its hydrophilic functionalization (S. Hu et al., 2021; T. Liu et al., 2016a). Considering its strong positive redox potential, quick charge transfer kinetics, high water solubility (high storage capacity), and superior structural stability, TEMPO derivatives are particularly desirable as catholyte candidate materials for aqueous RFBs (Alotto et al., 2012; Chai et al., 2020; B. Hu et al., 2017; Janoschka et al., 2015).

This study examined the solubility of TEMPO catholyte solution in several electrolyte solutions, such as NaCl, KCl, KOH, and H₂SO₄. The solubility of TEMPO as active species in electrolytes is essential in determining the energy density produced in AORFB systems (Fischer et al., 2022). A few can increase the solubility of active species in several ways. In most cases, the solubility of both inorganic and aqueous organic molecules is influenced by the choice of counter-ion (Fischer et al., 2022). The results of TEMPO solubility in different electrolyte solutions can be seen in Figure 4. TEMPO is perfectly dissolved in 1 M NaCl solution, up to 0.1 M, and in 1 M KOH solution and 1 M H₂SO₄. Meanwhile, TEMPO solubility in KCl electrolyte solution is a maximum of 0.08 M because it is seen that the addition of TEMPO can no longer increase the solubility of TEMPO itself. In comparison to other electrolyte solutions (NaCl, KCl, and KOH), the solubility of TEMPO solution in the H₂SO₄ electrolyte solution is high, suggesting that the effect of salting out is minimal. Adding TEMPO to the saturated solution even causes a decrease in TEMPO due to deposition. This phenomenon follows previous research that found that the solubility of TEMPO at 0.5 M of KCl solution ranges from 0.79 M (W. Zhou et al., 2020). In general,
TEMPO solubility in NaCl, KCl, KOH, and H₂SO₄ electrolyte solutions rises with increasing TEMPO solution concentration. Supporting electrolytes and the functional groups of TEMPO as demonstrated by earlier research, TEMPO solution functions well as a catholyte in RFB. The chemical can be utilized in an aqueous redox flow battery (ARFB) because of its hydrophilic functionalization (S. Hu et al., 2021). For instance, 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (4-HO-TEMPO), a TEMPO molecule, has a high-water solubility of 2.1M, according to (T. Liu et al., 2016a). Then, as an example, they created RFB using 0.5M methyl viologen(+) 4-HO-TEMPO(+). It has been demonstrated that quaternization is a successful method for raising the redox potential and solubility. N,N,N-2,2,6,6-heptamethylpiperidin-1-oxyl (TMAP-TEMPO), a more stable compound that demonstrated an energy density of 12.0 WhL⁻¹ and a potential of 0.81 V in RFB. Furthermore, according to the same author, there is a risk to the stability of the battery during operation since the neutral TEMPO molecule might readily pass through the separator membrane from the positive to the negative side. According to (S. Hu et al., 2021) the battery stability can be enhanced by the quaternary ammonium cation by successfully preventing the molecule from crossing the anion exchange membrane (AEM) through the Donnan effect.

3.2 Solubility of Methyl Viologen Solution on various electrolyte solutions

A type of redox-active molecules known as viologen compounds, having two redox potentials, have been studied in previous years (DeBruler et al., 2016a; DeBruler et al., 2017). The results of the study of MV solubility in several different electrolyte solutions can be seen in Figure 5. In general, the solubility of MV varies greatly and is influenced by its electrolyte solution. The solubility in H₂O is relatively very low. It indicates that MV, under normal conditions, has low solubility. However, after the addition of an electrolyte solution in the form of 1 M of NaCl solution, the solubility of the MV increased to 0.25 M. At 1 M of H₂SO₄, the solubility of MV almost 0.3 M. It suggests the corresponding viologen compounds' hydrophilicity is decreased by the larger organic substituents on N atoms (Jang et al., 2021; T. Liu et al., 2016a). The color, solubility, and electrochemical characteristics of viologen molecules are influenced by counter anions and substituents (Jang et al., 2021). Similar trends reported in the previous research, by using nitrate as a counter anion to MV and forming new water-soluble methyl viologen diocation (MVDn), it can increase the solubility up to 3.5 M with good electrochemical reversibility (Jang et al., 2021). Meanwhile, other literature reported two reversible reductions that can be achieved using methyl viologen with bis(trifluoromethane)sulfonamide counter anion in a non-aqueous supporting electrolyte (B. Hu & Liu, 2018). Regarding solubility, there are two kinds of counter anion for viologen: hard bases in the Lewis sense (F⁻, Cl⁻, Br⁻, or I⁻) and comparatively big counter-anions (NO₃⁻, ClO₄⁻, BF₄⁻, or PF₆⁻). Depending on the solution conditions (aqueous or organic) and charge state (radical-cation or viologen-dication), the anions' effects on the solubility of viologen differ (Bird & Kuhn, 1981; Monk, 1999).

The solubility of MV anolyte solutions in several electrolyte solutions, such as NaCl, KCl, KOH, and H₂SO₄ will be discussed here. As already stated, the solubility of MV in electrolytes is essential in determining the energy density produced in the RFB system (Kwabi et al., 2020). Because of their great water solubility, inexpensive cost, synthetic tunability, fast electrochemical kinetics, and superior chemical stability at pH neutrality, viologen molecules are very attractive anolyte materials. The most reliable cycling performance to far has been shown by viologen-based neutral AORFBs, which are considered to be the cutting edge of organic redox flow batteries (Chai et al., 2020; DeBruler et al., 2017; B. Hu et al., 2018).

![Fig 4. TEMPO Solubility in various electrolyte solution](image)

**Fig 4. TEMPO Solubility in various electrolyte solution**

![Fig 5. MV solubility in various electrolyte solutions (1M)](image)

**Fig 5. MV solubility in various electrolyte solutions (1M)**
3.3 Conductivity Measurement of TEMPO Solutions on various electrolyte solutions

Ohmic losses in the charge-discharge processes are directly related to the ionic conductivities of the supporting electrolytes, which are the capacity to transmit supporting ions for electrical conduction. For larger power outputs and significant cost savings in electrode regions and many cells/stacks, conductive electrolytes are necessary. Strong electrolytes are supportive electrolytes that have high levels of ionization. At higher concentrations, smaller free ion sizes are typically associated with enhanced conductivities (Gong et al., 2014; Tang et al., 2022).

This paper studies the electrical conductivity of TEMPO solutions in several electrolyte solutions. It can be seen in Figure 6. In general, electrical conductivity has a varied trend. As in TEMPO solutions without electrolyte, its electrical conductivity decreases to a concentration of 0.06 M and then increases to above 70 μS/cm. Another study stated that tempo solution in the form (4-glycidyl oxy-2,2,6,6-tetramethylpiperidine-1-oxyl) (GTEMPO) has electrical conductivity in the range of 10^{-3} μS/cm to 1 μS/cm (Bhat et al., 2021). While the TEMPO used in this study was measured to have electrical conductivity at a TEMPO concentration of 0.02 M to 0.1 M is 50-75 μS/cm.

Meanwhile, TEMPO in KCl electrolyte solution has an electrical conductivity value of 138 to 144 μS/cm, TEMPO in KOH electrolyte solution has an electrical conductivity value of 153 to 166 μS/cm, TEMPO in NaCl electrolyte solution has an electrical conductivity value of 99 to 118 μS/cm, TEMPO in H_2SO_4 electrolyte solution has an electrical conductivity value.

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**Fig 6.** Electrical conductivity of standard TEMPO solutions (a), and in electrolyte solutions KCl (b), KOH (c), NaCl (d), H_2SO_4 (e)
Electrical conductivity is influenced by how many ions are contained in the solution. Electrolyte solutions such as KCl, KOH, NaCl, and H$_2$SO$_4$ help to improve electrical conductivity, which can support the increased charging and discharging capacity of AORFB. From several electrolyte solutions tried, using a 0.1M H$_2$SO$_4$ electrolyte solution can significantly improve electrical conductivity from TEMPO up to 501-567 μS/cm. Ionic conductivities generally rise with supporting electrolyte concentrations; however, depending on the electrolytes, the effects of active material concentration on conductivities might vary greatly (Gong et al., 2015).

3.4 Conductivity Measurement of Methyl Viologen Solution on various electrolyte solutions

One factor that largely affects the ohmic resistance and, consequently, the discharge power density of an electrolyte system is the ionic conductivity of the electrolyte. The ionic composition of the electrolyte has a close correlation with the ionic conductivity (Fischer et al., 2022). The results of the study of the electrical conductivity of MV solution in several different electrolyte solutions can be seen in Figure 7. In general, electrical conductivity has a varied trend. As in MV solutions of 501 to 567 μS/cm.
without electrolytes, their electrical conductivity increases with an increase in concentration, starting from 1670 μS/cm at a concentration of 0.02 M and then rising to 6880 μS/cm at 0.1 M. The mobility of the hydronium/hydroxy ions is restricted at increasing concentrations because more water molecules are bonded to the counter ion. Moreover, the viscosity of the solutions increases and influences the ionic conductivities (Fischer et al., 2022).

In contrast to TEMPO solutions, adding electrolyte solutions such as KCl, KOH, NaCl, and H2SO4 decreases electrical conductivity in MV solutions. The decrease is quite significant; MV in KCl electrolyte solution has an electrical conductivity value of 14 to 17 μS/cm, in KOH electrolyte solution the electrical conductivity value of 194 to 202 μS/cm, in NaCl electrolyte solution has an electrical conductivity value of 85 to 100 μS/cm. In an electrolyte solution, H2SO4 has an electrical conductivity value of 219 to 232 μS/cm, respectively. Intermolecular contact is the origin of these occurrences because it modifies the ionic conductivity and transference number of electrolytes (Leverick & Shao-Horn, 2023).

3.5 Effectivity of the AORFB for Solar Energy Storage System

The RFBs system with a TEMPO solution of 0.1 M combined with 0.1 M H2SO4 as the catholyte and 0.1 M methyl viologen as the anolyte, as stated in the previous sub-section produces a fairly high conductivity compared to other variables, then tested on a solar energy storage system harvested through solar panels. In this study, 2 pieces of 10 W solar panels were used with a maximum current of 0.57 A and a maximum voltage of 17.8 W. Sunlight harvesting was carried out in the morning at 09.00 – 12.00 WIB every day. The measured current increase over approximately 35 minutes can be seen in Figure 8.

The process that occurs is the exchange of ions between catholyte, namely TEMPO solution, and anolyte, namely methyl viologen solution. TEMPO undergoes an electron addition reaction that causes TEMPO to change to TEMPO- which is characterized by a colour change from dark orange to light orange. Methyl viologen changes to Methyl Viologen2+ which is characterized by a colour change from light yellow to dark green, as seen in Figure 9.

The same phenomena were reported Liu et al, 2016 in the AORFB system of MV and TEMPO in NaCl solution (T. Liu et al., 2016b). During charging process, in the anolyte system, the MV solution is oxidised by donating electrons through an electrode and convert the MV to become radical cations MV2+. The reaction further exhibits colour change of the MV solution from light yellow into dark green. Meanwhile in the catholyte system, the TEMPO solution also received one electron turning TEMPO into its radicals TEMPO-. The reaction is noticeable by the colour changing from dark orange into lighter orange.

4. Conclusion

Analysis of the effectivity of the electrolyte in the AORFB system has been carried out. The investigation found that TEMPO solutions with high solubility can be achieved quickly, and the dissolved amount is not increased or reduced. As for methyl viologen (MV), the result is still below the expected solution concentration, even with several types of electrolyte addition. An electrical conductivity analysis has also been carried out. The results found an influence of the acquisition of electrolyte solutions on TEMPO catholyte and MV anolytes. In TEMPO solution, the addition of electrolyte solution can increase electrical conductivity, which can later increase the effectiveness of charging and discharging of AORFB. Meanwhile, a different trend is found in MV anolytes, the addition of electrolyte solutions decreases their electrical conductivity, so for the effectiveness of AORFB in anolytes, there is no need to add electrolyte solutions. The optimum condition for effective charge transfer in AORFB is TEMPO catholyte and MV anolytes in the 0.08 M H2SO4 electrolyte solution. RFBs systems can be used to store solar energy with a maximum current of 0.6 A for 35 minutes. Storage effectiveness is characterized by a change in colour in the catabolite and anolyte.

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Author Contributions:

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