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Study of Electrochemical stability of Anthraquinone derivative as Anolyte for Aqueous Redox Flow Batteries

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Abstract

Energy storage systems that are both cost-effective and highly efficient are essential for supplying a steady power supply from renewable resources. Redox-active organic molecules immersed in aqueous electrolyte can store energy in aqueous organic redox flow battery, a possible energy storage technology. This method has drawn a lot of interest as cost-effective and safe substitute for pricey commercial redox flow battery system. Here, we demonstrated a novel anolyte 4-((1, 4-dihydroxy-9, 10-dioxo-9, 10-dihydroanthracen-2-yl) diazenyl) benzoic acid) having low molecular mass, highly soluble in an alkaline aqueous media. It has presented an appropriate charge-discharge capacity in an ambient setting when combined with potassium ferrocyanide as a catholyte achieving a cell potential of 1.05V. This study can pay focus on incorporating water functionalities of azo-based compound for a suitable voltage. The designed anolyte has achieved columbic efficiency 75%, with an average decay rate of 0.02% about 200 cycles. These results have shown remarkable electrochemical stability, long-term storage capacity in future redox flow battery.

Introduction

High global demand and fossil fuel consumption have paid more attention toward renewable energy sources. Wind and solar energies are most encouraging alternatives, but required insufficient storage capacity to store energy for long term applications[1, 2]. Electrochemical batteries emerged as most advanced energy storage applications due to their longer lifespan, wide versatility and high energy densities [3]. Redox flow batteries are promising option for their large scale energy storage because of their extended life cycle, operational safety and decoupled energy and power capacity[4, 5]. Among all RFB technologies, vanadium is the most economically viable and sophisticated battery, but high cost vanadium, corrosive nature of acidic electrolyte and environmental concern are obstacles that limit their applications[6]. Due to these issues, Researchers have paid special attention toward aqueous organic redox flow batteries. They have variable redox potential and high stability which utilize low cost, sustainable and structurally tunable organic molecule as redox active specie[7]. But, they have limited solubility in neutral aqueous medium. It often require co-electrolyte with acidic/alkaline medium for remarkable solubility and stability. Although, previously reported organic material exhibit issues like low solubility at high current, due to redox irreversibility and degradation pathways. However, Significant advancement have made to overcome these challenges by improving solubility, stability through molecular engineering (e.g functional group modification), modification in pH, incorporation of additives and buffers, modification in battery components (e.g electrodes , membranes)and condition to get optimum results at high current densities[8, 9]

The development of organic compound such as quinones, viologens and TEMPO derivative have demonstrated potential for achieving high reversibility, long–term stability and cost efficiency in aqueous media. Among these material, redox active molecule of anthraquinone have get more interest, because of their stable redox activity of $2e^-$, tunable redox potential and long-term stability in aqueous electrolyte[10]. The substituted anthraquinone derivative such as 2,6-DHAQ, 1,5-DHAQ exhibit wide pH range, strong electrochemical reversibility and varying redox potential, making them promising candidate as anolyte in AORFB[11]. Despite the advantages, pH dependent solubility, chemical stability problem, capacity loss during cycling and side reaction during prolonged cycling still hinder their practical deployment[5]. Azo and azo benzene redox active compound are promising candidate because of low cost availability and hydrophilicity. There is wide range of possibilities in molecular design by different functionalities, but have rare reports on their usage as electrolyte in redox flow battery[12, 13]. The high capacity in azo functionality is ensured by $2e^-$ reversibility in AORFBs. The hydrophobicity is caused by azo functionality's symmetry which imposed limited solubility in aqueous medium. The addition of hydrophilic group can enhance solubility in this regard. The stability of azo dye is a common concern by incorporating different functional group varying different stability. The dye 4-((1, 4-dihydroxy-9, 10-dioxo-9, 10-dihydroanthracen-2-yl) diazenyl) benzoic acid) is used in this study, carboxylic group (-COOH) and azo linkage of dye show remarkable stability as anolyte in redox flow cell. The dye retain its molecular structure and redox behavior after repeated cycling performance in AORFB[14].

Due to above gaps , we experimentally utilized dye named as (4-((1, 4-dihydroxy-9, 10-dioxo-9, 10-dihydroanthracen-2-yl) diazenyl) benzoic acid) have carboxylic functionality that efficiently enhanced the aqueous alkaline solubility of the diazenyl compound. For the first time , we have efficiently manufactured and performed on low molecular mass azo-based compound under undemanding surrondings. This novel compounds offered long-term cycling stability despite its intial cycle of low efficiency, shows significant promise for long-term sustainable large scale energy storage applications. Moreover, their cycling stability promotes reduced capacity losses, ultimately contributing to excellent electrochemical performance and lower system costs. Beyond the intial activation stage, the system exhibits exceptional stability having 75% columbic efficiency , with a minimum capacity degradation rate of just 0.021 % per cycle over 200 cycles. This study supports the incorporation of multifunctional diazenyl molecules, having high aqueous solubility, stability and reversible redox potential to function as anolyte in AORFBs for large-scale energy storage system.

Experimental section:

Chemicals and methods:

4-Aminobenzoic acid, Urea [$CO(NH_2)_2$], 1,4-dihydroxyanthraquinone , Sodium nitrite ($NaNO_2$), Sodium carbonate (Na_2CO_3), potassium hydroxide pellets (KOH) and Dowex-50W resin have been purchased from Sigma-Aldrich. Potassium hexa ferrocyanide K4 [$Fe(CN)_6$], Hydrochloric acid (HCl) were procured from Fisher Scientific Company (USA). The redox flow cell was fabricated by usage of Aquivion E-98-15S Membrane (Solvay, USA) and 3mm Graphite Felt electrodes (Qingdao Dongkai Graphite Co. Ltd).

Synthesis process of (4-((1, 4-dihydroxy-9, 10-dioxo-9, 10-dihydroanthracen-2-yl) diazenyl) benzoic acid)

The diazenyl compound **(fig 1)** has been prepared by a diazonium coupling reaction between 4-amino-benzoic acid and 1,4-dihydroxyanthraquinone. Here, 4-amino-benzoic acid has first converted into a diazonium salt using sodium nitrite and hydrochloric acid. Briefly, In a 2 neck-round bottom flask, 4-amino-benzoic acid (8.00mmol) was dissolved in hydrochloric acid (6.0M, 50.0mmol) and cooled in an ice bath (0-5°C). A cold aqueous solution of sodium nitrite was added drop-wise with constant stirring to form the diazonium salt. The reaction mixture was stirred for 30 minutes and excess nitrite was removed by adding a small amount of urea solution. Separately, 1,4 dihydroxyanthraquinone (7.00mmol) was dissolved in a cold alkaline sodium carbonate solution (14mmol in 15-20ml water). The diazonium solution was slowly added to this cold alkaline solution with continuous stirring. The resultant mixture was kept under stirring in an ice bath for 6hrs and left overnight at low temperature. The resulting product was filtered and dried in a vaccum oven at 60°C. The dye was purified by ion exchange column using Dowex 50W resin.

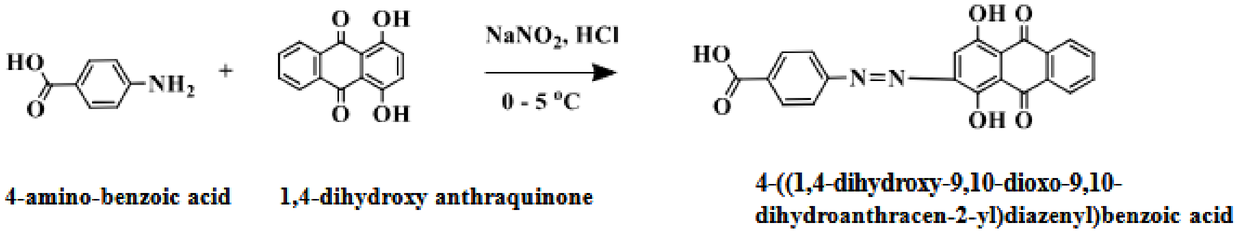

Fig 1: Synthetic pathway for (4-((1, 4-dihydroxy-9, 10-dioxo-9, 10-dihydroanthracen-2-yl)diazenyl) benzoic acid**.**

Characterization techniques:

Fourier transform infrared spectroscopy (FTIR) was done to verify the existence of functional groups that match the produced compound's predicted structure., carbon-13 nuclear magnetic resonance (^{13}C-NMR) provide more evidence in favor of the produced compound's suggested structure and proton nuclear magnetic resonance (^{1}H-NMR) identified successful synthesis of a compound and the hydrogen atoms are in predicted chemical environment.

Electrochemical characterization:

The redox behavior and electrochemical reversibility (cyclic voltammetry (CV)) of the synthesized material were examined by using computer-controlled three-electrode system (Auto-Lab PGSTAT-128N) via Nova 2.1.4 software. A glassy carbon working electrode, a platinum counter electrode, and an Ag/AgCl reference electrode in 1.0 M KOH electrolyte comprised the three-electrode system used for the measurement. All of the electrochemical performances were assessed using three-electrode setup. The electrochemical cell was made up of pyrex glass covered with Teflon, washed using H_2SO_4, boiled in deionized water, and then dried in an oven.. The results were obtained after argon was purged from the electrolyte solution for 15 minutes to eliminate the air bubbles. Four to five repetitions of these tests were conducted for accuracy and reproducibility. All measurements were collected at room temperature Electrochemical experiments were conducted using redox-active solutions at a concentration of 1 mM in 1 M KOH as the electrolyte. The electrochemical behavior of species was investigated using cyclic voltammetry at scan rate of 30mv/s in 1M KOH. The combined potential of the full cell shows an open circuit voltage of 1.05 V. The voltammogram of the resultant data showed the stable redox behavior and effective electron transport make the material a viable option for redox flow battery applications.

Redox flow cell set up:

The redox flow cell (Scribner Associates, USA) **(Fig 2)** has been assembled by graphite bipolar plates, Viton rubber gasket and Teflon flow frame plates. Carbon-felt electrodes were used both as an anode and cathode. An Aquivion E98-15S membrane (Solvay, USA) served as ion exchanger. The Aquivion E98-15S membrane was pre-treated by soaking in a 1M KOH solution (at 70°C for 8 hours). Pre-treated Aquivion membrane was sandwiching between two pre-oxidized carbon-felt electrodes. Each electrolyte was prepared by dissolving the material in 1M KOH (25mL) before anolyte (0.05) and catholyte potassium hexa ferrocyanide (0.01M) were used. The Peristaltic Pump was used to circulate electrolyte at flow rate of 100ml/min. Charge-discharge cycling was performed at constant current of 50 mA with in voltage of 0.2-1.8V. Electrochemical performance was done by a Neware battery testing system equipped with BTS Software (version8.0.0).

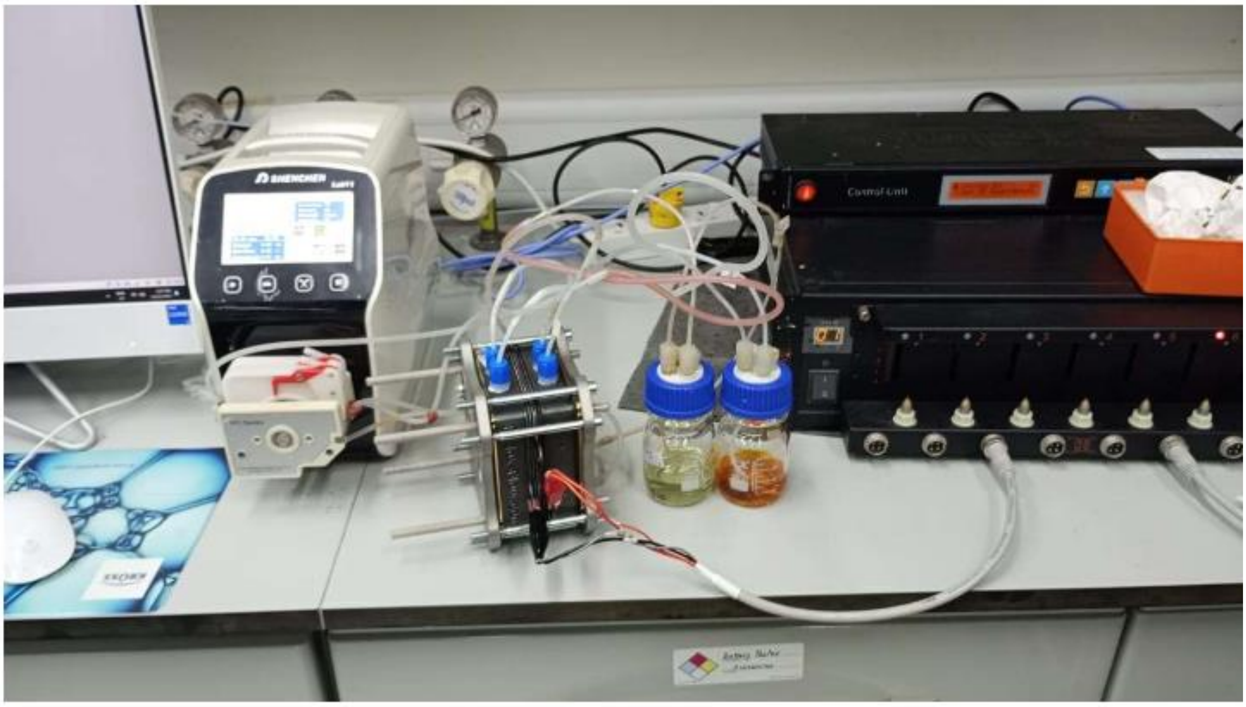

Fig 2: AORFB testing experimental setup, displaying electrolyte tanks, pumps, tubing, flow cell, and monitoring apparatus.

Result and Discussion:

Characterization of synthesized compound:

The functional group of the synthesized compound was investigated by using FTIR as shown in (**fig3**). In FTIR spectrum, the peak was observed at 1688cm^{-1} relate to the conjugated peak of carbonyl functionality. Stretching vibrations C=C were observed at 1627-1588cm^{-1} indicate the presence of benzene ring. The presence of peak at 1452cm^{-1} suggested a presence of saturated hydrocarbon. Moreover, the low frequency peaks appeared at 1254cm^{-1} and 1212cm^{-1} supported the presence of heteroatom (C-O) and (C-N). FTIR analysis revealed the molecular structure of the synthesized compound

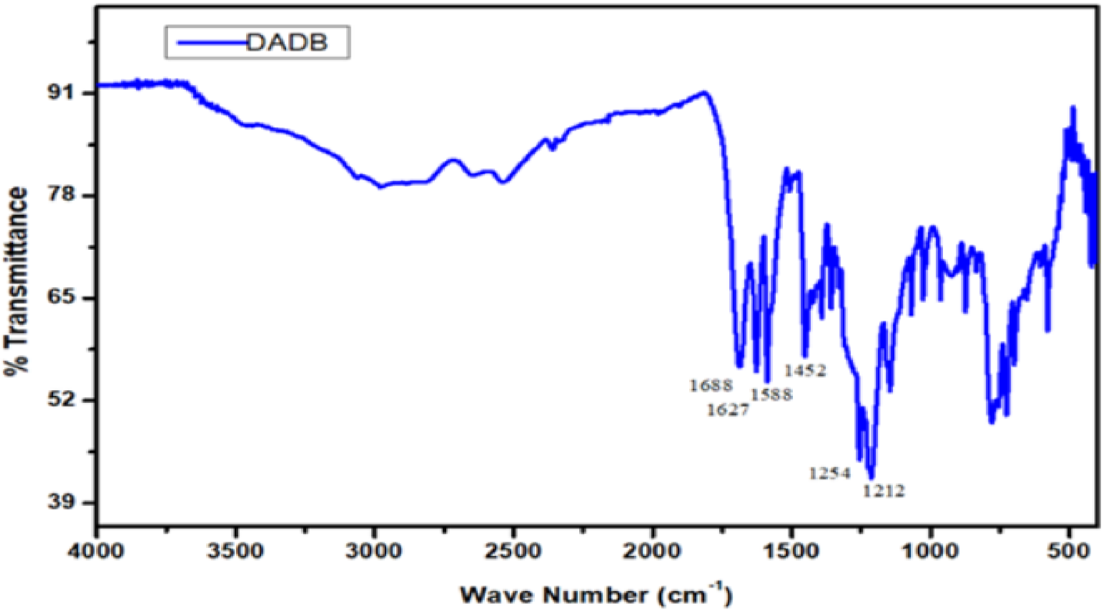

Fig 3: FTIR spectrum of the anolyte (4-((1,4-dihydroxy-9,10-dioxo-9,10-dihydroanthracen-2-yl)diazenyl)benzoic acid.

.**(Fig4)** show the ^{13}C-NMR spectrum of the synthesized compound The ^{13}C-NMR spectrum of the compound verify the purified dyes of the synthetic compound by showing peaks at ^{13}C NMR (75 MHz, DMSO-d6) δ: 185.46, 184.82,168.80, 162.04, 157.28, 152.00, 141.38, 133.95, 133.37, 133.24, 131.80,131.00, 126.77, 126.73, 121.38, 114.47, 114.00, 109.64. ^{13}C-NMR spectrum gives more evidence in favour of structure to synthesized the compound.

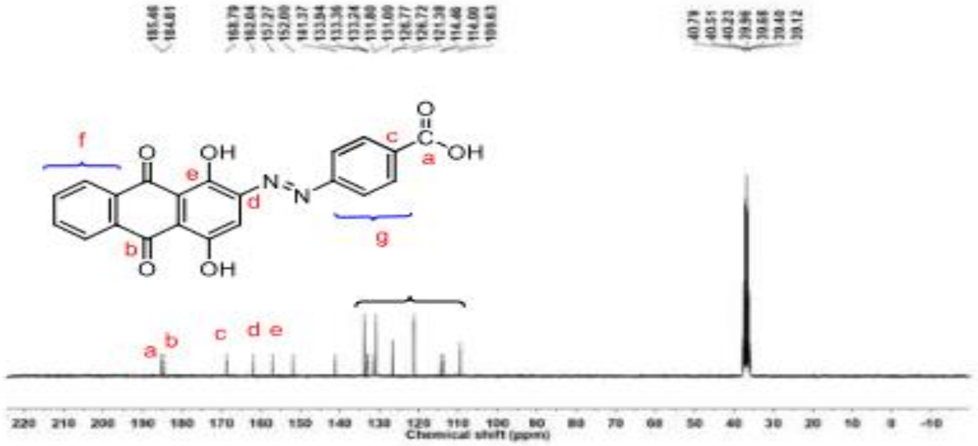

Fig4: ^{13}C-NMR spectrum of the anolyte (4-((1,4-dihydroxy-9,10-dioxo-9,10-dihydroanthracen-2-yl)diazenyl)benzoic acid.

^{1}H-NMR spectrum **(fig5)** reveals successful synthesis of a compound with hydrogen atoms in a predicted chemical environment by showing peaks at 1H NMR (300 MHz, DMSO-d6) δ: 14.00 (s, 1H), 13.65 (s, 1H), 12.91 (s, 1H), 8.35 – 8.17 (m,4H), 7.95 (d, J = 7.5 Hz, 2H), 7.85 (dd, J = 5.7, 3.8 Hz, 2H), 7.45 (s, 1H).

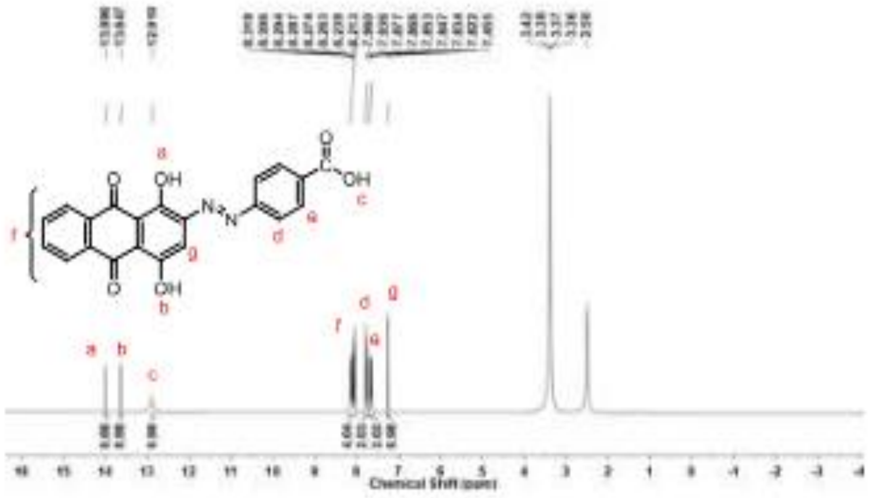

Fig 5: ^{1}H-NMR spectrum of the anolyte (4-((1,4-dihydroxy-9,10-dioxo-9,10-dihydroanthracen-2-yl)diazenyl)benzoic acid

From the last decade, organic functional groups play a critical role in designing these species, particularly in organic RFBs which offer advantages like tunability, low cost and reduced environmental impact as compared to inorganic counter parts. The carbonyl (C=O), Sulphide (S), Azo groups are among key functional moieties explored for their redox activity. Azo compounds are characterized by -N=N- functional group, are emerging an promising redox active material in aqueous organic redox flow batteries. These batteries store energy in liquid electrolyte containing organic molecule dissolved in water, offering advantage like sustainability and low cost compared to traditional inorganic system like vanadium redox battery. Azo compound serve as the redox-active specie in the anolyte, enabling electron transfer to store and release energy.

Organic redox flow batteries (RFBs) rely on the azo (–N=N–) group, a redox-active functional unit, to facilitate electron transport. The N=N double bond can undergo reversible reduction and oxidation during charge-discharge cycles due to its delocalized π-electron system. The azo linkage exhibits a stable two-electron redox mechanism when it accepts two electrons in its reduced state to create a hydrazo (–NH–NH–) species, which can subsequently be oxidized back to the azo form in subsequent cycles[15]. This reversible N=N ↔ NH–NH transformation promotes rapid charge transfer at the electrode–electrolyte contact and offers a high electron density. They make them suitable for green AORFBS where they can pair with Potassium ferro cyanide to achieve cell voltages 1.1-2.0V and high energy densities. The redox reaction in Azo compound center on -N=N- group, leading to reversible structural changes that enable energy cycling[16]. These changes are characterized by spectroscopy (1H-NMR, 13C-NMR & computational methodology. Numerous organic electrolytes that have been optimized, including viologens, anthraquinone, and quinone, show strong reversibility in some derivatives. However, in order to maximize the potential of azo-based systems, co-electrolyte, pH, and stabilizing agents that can reduce the irreversible electrochemical breakdown pathways must be selected.

Redox flow cell performance:

The galvanostatic charge-discharge performance of the redox flow battery was observed at constant current density of 10mA/cm^2 for 200 cycles, in the voltage range of 0.3V-1.5V under ambient atmospheric condition. An alkaline medium are necessary for the solubility of anthraquinone, while the addition of 1g Urea and KCl improved the stability and conductivity of anolyte, respectively. The cell shows stable first cycle performance with a charge and discharge capacity of 60.4 mAhL^{-1} and 37.2 mAhL^{-1} showing a coulombic efficiency (CE) of 61.5%. This relatively low efficiency in the intial cycle was related to internal ohmic resistance, initial stabilization, electrode-electrolyte contact and slight side reactions associated with surface activation of electrode [44, 45]. In the subsequent cycles the capacity stabilization effect has been noted with a second cycle charge- discharge capacity of 56.2 mAhL^{-1} and 42.7 mAhL^{-1} with a CE of about 76 %, indicating the reduced internal ohmic resistance and enhanced redox reaction reversibility. The cell (**fig6)** shows stable performance in the extended cycling for 200 cycles with consistent charge-discharge behavior and an average CE of around 75%. The charging voltage of ~ 1 V also reflects a good match with the theoretical open circuit voltage of 1.05 V, confirming efficient electrochemical ehavior.

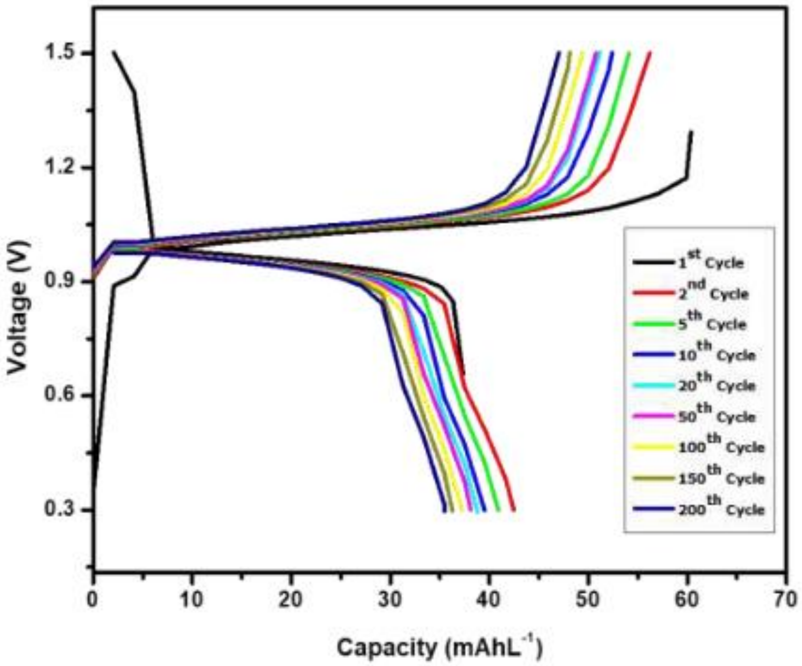

Fig 6: Charge-discharge profile of full cell.

The electrochemical performance of electrode was further evaluated through term cycling test.as shown in **(fig. 7),** the electrode delivered an initial discharge capacity of 37.2mAhL^{-1} and retained 35.4mAhL^{-1}, after 200 cycle related to the 95.2% capacity retention. But in the intial cycle, some drop capacities in both charging and discharging was observed refers to electrolytic chemical change, cross-over species and oxygen impurities. Moreover, columbic efficiency remained nearly constant at 75% at about 200 cycles. These results shown strong cycling durability of electrode and remarkable electrochemical stability, making it a extraordinary candidate for long term energy applications.

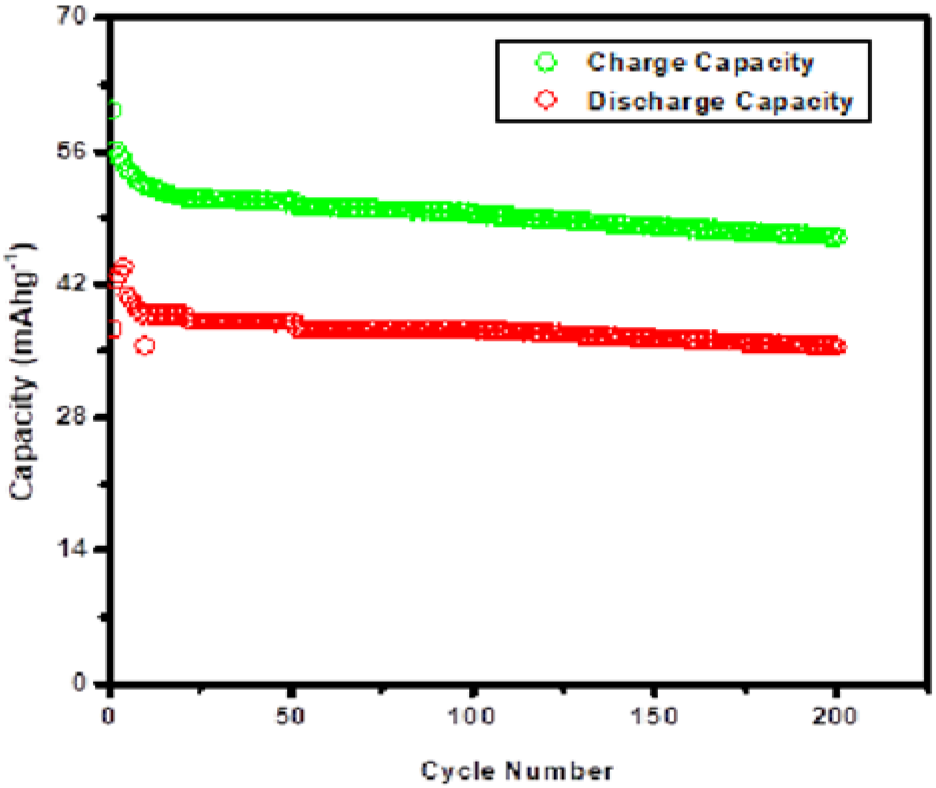

Fig 7: Charge-discharge cycling of the redox cell over 200 cycles showing stable performance.

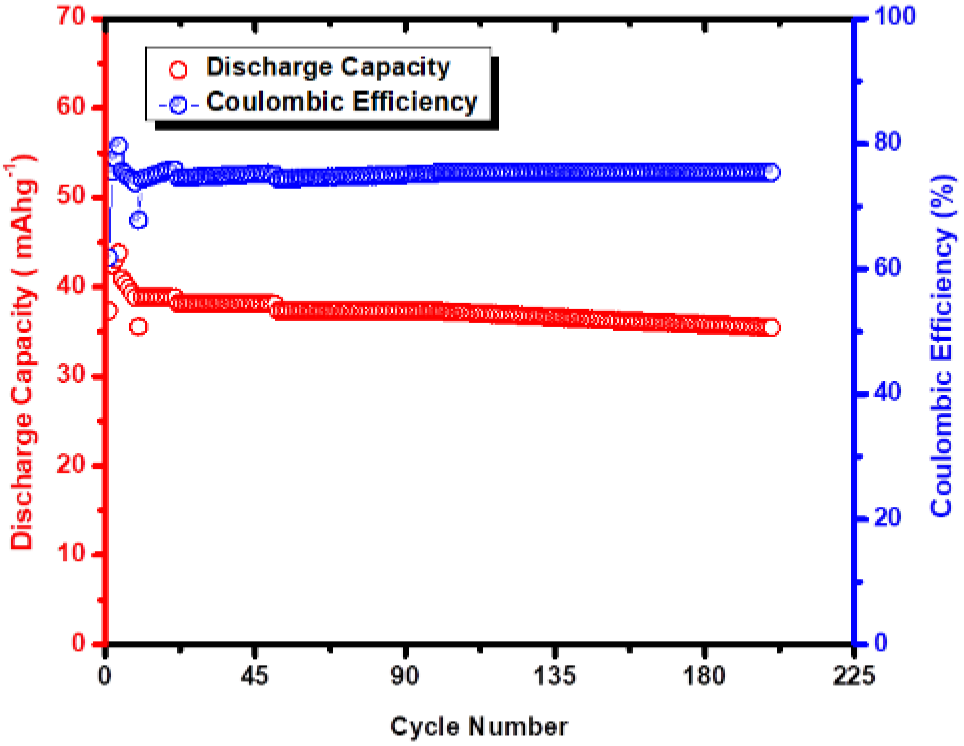

Fig 8: Discharge capacity and columbic efficiency plots.

Electrochemical behavior:

Cyclic voltammetry **(fig 9)** was conducted using 0.1M anolyte and catholyte solution, by employing an Ag/AgCl reference electrode, a Pt counter electrode and a glassy carbon working electrode in a 3-electrode configuration at scan rate of 30mvs^{-1}.

The redox behavior of DADB anolyte exhibited a distinct redox peak at –0.67V, corresponding to the principle electron transfer process N-N reduction in this potential range [16]. The catholyte $[K_4Fe(CN)_6]$ displayed a characteristics oxidation peak at approx. 0.38V, consistent with well known Fe^{2+}/Fe^{3+} redox couple. The combined redox potential of DADB anolyte and $[K_4Fe(CN)_6]$ catholyte yield 1.05V of an open-circuit voltage (OCV), confirming the theoretical compatibility of the redox pair. The well-defined and reversible redox peaks, along with the narrow potential separation, indicate fast electron transfer kinetics and high electrochemical reversibility, validating the suitability of DADB as a promising organic anolyte and redox application.

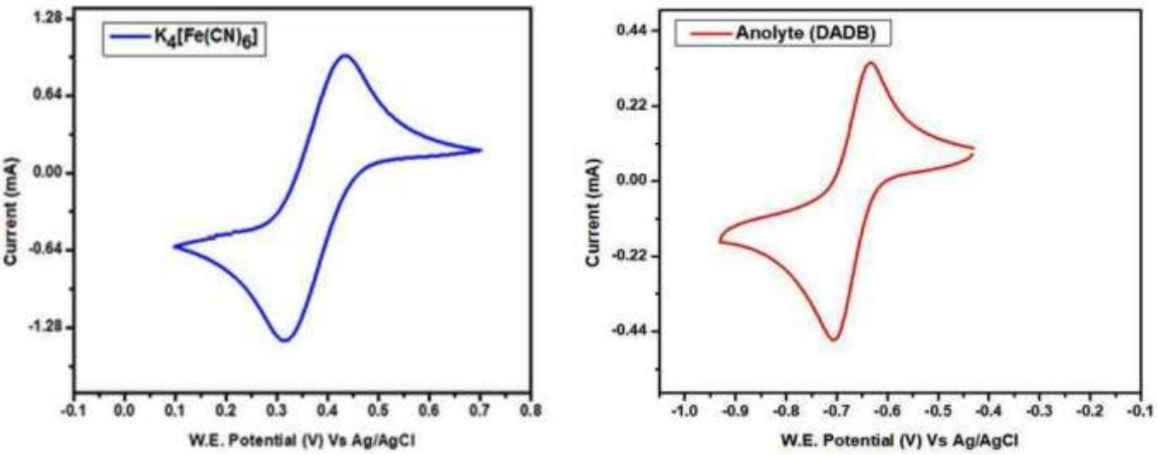

Fig 9: CV of anolyte and catholyte at scan rate of 30 mVs-1 suggest a theoretical open circuit voltage of 1.05V.

Overall, good electrochemical stability and 75% Coulombic efficiency were indicated by the cell's consistent capacity retention, along with a few side reactions. Despite the fact that the cells CE is not very high, it may indicate that species crossing-over has occurred. Overall, the electrochemical and post-cycling analyses confirm that both anolyte and the catholyte exhibit good reversibility, minimal volume change and satisfactory chemical stability even after extended cycling, with only minor color changes due to electrolyte imbalance, a balance between oxidized and reduced forms diverges due to crossover or insufficient reversibility, is commonly observed in post-cycled electrolytes. So, the electrolyte conductivity may wander as a result of supporting ion depletion during cycling, cause slight color variation. Overall, they are indicating robust long term performance in RFB applications.

Conclusion:

Azo-based radioactive molecules have wide applications due to their low cost , long-term cycling stability and enhanced aqueous solubility, which can be adjusted according to functional groups. The anolyte (DADB) was synthesised and characterized by using spectroscopic technique such as NMR and FTIR. The anolyte have shown 75% columbic efficiency and 0.021% average decay per cycle under ambient cycling conditions. Moreover, they have wide possibilities in molecular design due to different functionalities. There are still not reported their usage as electrolyte in redox flow batteries. The results demonstrate that low molecular mass azo- based electrolyte can be effectively engineered by changeable functionalities of azo derivative, enhanced their applications in AORFB operated under non-demanding ambient conditions. Moreover, results can be enhanced by modification in electrodes, electrolytes, membranes and additives. Overall, these advancement provides a new insight into advancement of different functionalities in different organic electrolyte and provide a base for future advancement of cost effective and efficient aqueous redox flow batteries .

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