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Functionalised carbazole as cathode for high voltage non-aqueous organic redox flow battery

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Abstract

Prospective high reduction potential cathode material has been proposed that can be used in nonaqueous redox flow battery application. New class of material, 3,6-dibromo-9-(p-tolyl)-9Hcarbazole (3) incorporating carbazole core, showing a very good reversibility is employed as the cathode material and dissolved oxygen in the solvent mixture is used as the anolyte material. Labile positions of the carbazole have been substituted with the electron withdrawing groups, which increases the reduction potential of the redox couple. Apart from substituting the labile positions, we have also explored the possible structural modification responsible for stabilizing the cation radical of carbazole moiety and obtained the reversible behavior thereafter. From this, it is evident that free radical is stabilized upon delocalization of the charge in the molecule. The mass-transport and redox parameters, diffusion coefficient and heterogeneous electron transfer rate coefficient values are high enough to realize good battery performance. A solvent mixture of acetonitrile and dichloromethane (4:1) has been used in this work in order to increase the solubility of electroactive material in the medium.

Keywords: 3,6-dibromo-9-(p-tolyl)-9H-carbazole; oxygen/superoxide redox couple; acetonitrile and dichloromethane electrolyte mixture

There is a great demand for the storage of electrical energy generated by the renewable sources

1. Introduction

 due to intermittent nature of these sources. In flow batteries, energy is stored in the charged liquids unlike conventional rechargeable batteries where energy-storing species are embedded on the electrode structure and discharged as per demand as the charged solution flows through the electrode. As a result, there is spatial separation between electrode structure and electroactive material leading to decoupling of energy and power. So, energy and power can be independently varied by modulating size of the solution tank for the former and the electrode area for the latter, respectively ¹. So far, vanadium redox flow battery (VRFB) have undergone thorough research and also been commercialized in some places ². But, it also suffers from the inherent limitation of offering a limited potential window for operation as water can be electrolyzed at the potentials of operation and readily available vanadium which in turn leads to high cost of VRFB operation ³. So, the use of non-aqueous medium having higher electrolyte decomposition voltage with suitable redox couple offers larger operational potential window, which can increase the energy density of the battery considerably.

In the case of metal containing batteries the lack of metal abundance, scarcity of technology readiness and environmental concerns involving disposal of used battery materials capped the growth at certain stage. So there is a growing demand for energy storage devices, which show least impact on the environmental crisis. Non-aqueous organic redox flow battery (NAORFB) meets this requirement since it uses less-polluting and bio-degradable electroactive organic materials for its making and so requiring less attention for its disposal. In the current scenario, a number of class of organic compounds (ketones, quinones, phenazines, phthalimides, 2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO), alkoxyarenes etc.) showing reversible electrochemical

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behavior have been used ^{4–11}. In a bid to expand the domain of materials capable of showing better energy density with higher redox potential for NAORFB, we have come up with carbazole substituted species as one of the electrode materials. Derivatives of carbazole look promising as they form stable cation radicals due to planarity of the aromatic carbazole ring and are explored in a number of applications like electrophotographic photoreceptors, photorefractive materials, light emitting diodes and photovoltaic devices owing to the ease with which they can transport positive charges ^{12–16}. In all these applications, photoconductive properties of carbazole containing polymers are used which exploit the ability of these polymers to transport positive charges, as the formed positive charges are stable. Mikawa et al. have transformed insulating and non-conjugated pendant poly(vinylcarbazole) polymer into electrically conducting polymer by electrochemical doping as these are stable and used them as positive electrode material in Li-ion battery applications ¹⁷. This was an enough motivation for us to look for carbazole derivatives as catholyte material. Carbazoles are attractive for employing in organic redox flow battery as they can be modified with suitable substituent to enhance their solubility in a given solvent which directly affects capacity and so energy density of the battery ^{18,19}. We can improve the reversibility of electrode material by substituting the chemically labile positions with stable substituents which otherwise would yield a number of side reactions by reacting with the cation radical formed ^{20,21}. Blocking 3 and 6 positions of carbazole yields quite a stable cation radical ²². Moreover, by substituting with suitable functionality, redox potential could be varied towards higher open circuit voltage of the battery ¹⁹. We have chosen (3), as carbazoles lend flexibility to tune properties such as solubility, redox potential, reversibility of the redox species by introducing appropriate substituents. Moreover, carbazole is an economically viable option as it is obtained as the byproduct of distillation of coal tar, which in turn can be used to synthesis a number of carbazole derivatives.

2. Experimental

2.1. Materials

(3) was synthesised from carbazole (1) as the starting material which was purchased from Spectrochem chemicals. L-proline, p-bromotoluene, CuI, K_2CO_3 , N-bromosucciniide, acetic acid and 9-ethyl-9H-carbazole was purchased from TCI chemicals (India) Pvt. Ltd. Tetrabutylammonium hexaflurophosphate (TBAPF₆) was purchased from Sigma-Aldrich. Dimethylformamide (DMF), toluene, dimethylsulfoxide (DMSO), acetonitrile (ACN) and dichloromethane (DCM) were obtained from Fisher Scientific Ltd. Graphite felt was obtained from Nickunj Eximp Entp Pvt. Ltd. and Celgard 2320, polypropylene based porous membranes were procured from Celgard North Carolina. Nitrogen (N₂) and oxygen (O₂) gases were procured from Indogas agency, Chennai, India.

2.2. Synthesis of 3,6-dibromo-9-(p-tolyl)-9H-carbazole

N-Arylation of (1) was carried out using Ullmann reaction condition. To the mixture of (1) (1.3 g, 7.77 mmol, 1 equiv), L-proline (90 mg,0.77 mmol, 0.1 equiv), p-bromotoulene (1.4 mL, 10.88 mmol, 1.4 equiv), CuI (148.1 mg,0.77 mmol, 0.1 equiv), $K_2CO_3(2.15 \text{ g},15.55 \text{ mmol}, 2 \text{ equiv})$ and 24 mL of DMSO as solvent was added and refluxed for 24 h. The product obtained from the reaction mixture was filtered by adding excess of cold water. 9-(p-Tolyl)-9H-carbazole (2) was purified from the mixture by silica gel column chromatography using hexane as solvent and then dried to get pure compound. To chilled 10mL of 0.5 mM solution of (2) in DMF, N-bromosuccinimide corresponding to 1.1 mM (0.2 g) was added. The mixture was stirred at room

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temperature for 3 hours. Ice was added to the mixture to give a white precipitate. After drying, the solid was recrystallized using toluene to obtain pure compound of (3).

9-(p-Tolyl)-9H-carbazole (White solid) :¹H NMR (400 MHz, CDCl₃) δ 8.06 (d,2H), 7.36-7.28 (m, 8H), 7.21 – 7.16 (m, 2H), 2.40 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 141.2, 137.5, 135.1, 130.6, 127.1, 125.9, 123.3, 120.4, 119.8, 109.9, 77.2; HRMS (ESI): Calcd. For C₁₉H₁₅N [M+H]⁺ 258.1277; found = 258.1279 (**Fig. S1 – S4**).

3,6-dibromo-9-(p-tolyl)-9H-carbazole (White solid) :¹H NMR (400 MHz, CDCl₃) δ 8.11 (s, 2H), 7.42 (d, 2H), 7.33, 7.29 (dd, 4H), 7.15 (d, 2H), 2.41 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 140.2, 138.3, 134.2, 130.8, 129.4, 126.9, 123.9, 123.3, 113.0, 111.6, 77.2; HRMS (ESI): Calcd. For C₁₉H₁₃Br₂N [M+H]⁺413.9373; found = 414.9393 (**Fig. S5 – S8**).

2.3. Synthesis of 3,6-dibromo-9-ethyl-9H-carbazole (4)

A mixture of 9-ethyl-9H-carbazole (1 g, 1 equi), N-bromosuccinimide (1.8 g, 2 equi), toluene (1 ml, 1.75 V) and acetic acid (3 ml, 7 V) were stirred overnight. Reaction was monitored by thin layer chromatographic technique to ensure the completeness. At the end of reaction, the mixture was evaporated to remove Br_2 . The solid residue obtained upon evaporation was purified by column chromatography on silica gel by using mixture of hexane/ethyl acetate (98 : 2) as an eluant.

3,6-dibromo-9-ethyl-9H-carbazole (4) (White solid) ; ¹H NMR (400 MHz, CDCl₃) 8.16 (s, 2H), 7.59, 7.57 (dd, 2H), 7.29 (d, 2H), 4.33 (q, 2H) and 1.42 (t, 3H) ; ¹³C NMR (100 MHz, CDCl₃) δ 138.8, 129.0, 123.6, 123.3, 111.9, 110.2, 37.9, 13.7 ; HRMS (ESI): Calcd for C₁₄H₁₁Br₂N [M+H]⁺ 352.9312; found = 353.9302 (Fig. S9 – S12).

2.4. Electrolyte preparation and cell fabrication

 5 mM solution of (3) in 4:1 (v/v) solvent mixture of acetonitrile (ACN): dichloromethane (DCM) with 0.1 M TBAPF₆ was prepared to act as catholyte. Similarly O_2 was dissolved in the solvent mixture of 4:1 (v/v) of ACN : DCM to act as anolyte with 0.1 M TBAPF₆ as the supporting electrolyte as well as the stabilizer of superoxide ²⁰. The cell was assembled as shown in the schematic diagram (Fig. 1). The order of components of the half-cell: SS endplate, copper current collector, carbon block with a well of 6 mL volume, silicone rubber gasket of 3 mm thickness with a pocket of size 2.7 cm x 2.7 cm wherein activated carbon felt is to be placed. The well is connected to the pocket with perforations to deliver the reactants from the well.



Fig. 1 Schematic representation of the assembled cell using (3) as catholyte and O_2 / TBAPF₆ as anolyte.

 Two such half cells are placed on either sides of the Celgard porous separator, which makes the complete cell. The entire assembly is compacted using bolts and nuts. The solution in the anode compartment was kept in contact with the oxygen atmosphere using the oxygen filled balloon.

2.5. Electrochemical characterisation

Three electrode mode CV studies were carried out using Biologic VSP potentiostat. A glassy carbon electrode of 0.196 cm² area and Ag/Ag⁺ (10 mM AgNO₃ in ACN) were used as working and reference electrodes respectively. Pt mesh was used as the counter electrode. The cation radicals of (1), (2) and (3) are labelled as (1⁺), (2⁺) and (3⁺) respectively. Similarly polarisation studies were carried out by linear sweep voltammetry for the determination of exchange current density (*i*₀) of the redox couple (3)/(3⁺) using rotating disk electrode (RDE) as the working electrode. The glassy carbon RDE with a disk diameter of 5 mm obtained from PINE instruments was used. 5 mM solution (3) and oxygen saturated ACN:DCM (V/V 4:1) solutions were used to record the Nyquist plot at 1.09 V and -1.24 V vs. Ag/Ag⁺, respectively with a 5 mm diameter glassy carbon working electrode. 0.1 M TBAPF₆ was used as the supporting electrolyte. Frequency range employed in recording Nyquist plot is 100 kHz to 0.1 Hz with a voltage perturbation of 10 mV. The kinematic viscosity of the reaction medium was measured using Anton-Paar Lovis2000 M/ME Microviscometer at 25°C for determining diffusion coefficient using Levich equation.

3. Results and discussion

3.1 Cyclic voltammetry

Cyclic voltammetry was performed using (1), (2), (3), and (4) to understand the extent of reversibility of the redox process. Fig. 2(a) and (b) compares the 3rd and 60th cycle of (1) and (2).



Fig. 2 (a) and (b) shows the CV of (1) and (2) in 4 : 1 Solvent mixture of ACN : DCM containing 0.1 M TBAPF₆ as supporting electrolyte respectively in their 3^{rd} and 60^{th} cycles.

(1) shows some redox activity for initial few cycles and loses it when cycled 60 times expectedly due to the formation of unstable cation radical (1^{+.}) and unknown polymer coating on the electrode surface which blocks the availability of electrode surface for further reaction 21 . When 9-H proton of (1) was substituted with tolyl group (**Fig. 2b**) moderate retention of redox activity was witnessed even after 60th cycle though there is decrement in the peak current due to the free availability of chemically labile 3rd and 6th positions in the carbazole core for dimerization. The quasi-reversible oxidation peak obtained for (2) around 0.95 V is due to removal of an electron from the lone pair of N yielding cation radical which may undergo dimerization 22 . The redox peak obtained around 0.6 V is due to the oxidation of dimer of (1) and (2). The 3,6 positions in (1) being highly susceptible to electrophilic substitution can easily undergo electrochemical oxidative polymerization during cycling making the redox reaction irreversible²². So, blocking these positions is important to obtain electrochemical reversibility. Here bromine being an electron withdrawing group shifts the onset of oxidation potential to more positive value ²².



Fig. 3 (a) and (b) shows CV of (3) and (4)) in 4 : 1 solvent mixture of ACN : DCM containing 0.1 M TBAPF₆ as supporting electrolyte, respectively in their 1^{st} , 2^{nd} and 100^{th} cycle.

(3) yields a stable reversible redox signature $(3/3^+)$ for a very large number of cycles (100 cycles) owing to the formation of stable cation radical (Fig. 3a). Since cation radical is formed initially at the N centre of carbazole core, role of different N-H substituent in stabilizing the cation radical formed can also be evaluated. Hence, 1st, 2nd and 100th cycles of (3) and (4) are compared in Fig. 3(a) and (b) respectively. CV curves of (3) in their 1st and 100th cycle are overlapping one over the other indicating the reversible and stable cation radical formation. Formation of stable cation radical can be attributed to the resonance stabilisation of cation radical by the tolyl group substituent. There is gradual decrease in the peak current of (4) while moving from 1^{st} cycle to 100th cycle indicating the relatively unstable nature of the carbocation formed ²². This is possibly due to the absence of resonance stabilization by the N-ethyl group. Hence, an aromatic substituent is the most suitable moiety for stabilizing the cation radical formed. Nitrogen of carbazole moiety is capable of showing both inductive and mesomeric effect by virtue of being electronegative and possessing lone pair of electron on it, respectively. Although the electronegative N atom in (3) destabilizes the cation formed, the cation radical is stabilized more through mesomeric effect offsetting the inductive effect. Substitution of tolyl group at the 9th position stabilizes the cation

 formed more compared to substitution by ethyl group further by resonance effect. Also, substitution of more electron withdrawing group like tolyl group, imparts higher $E_{1/2}$ (by 50 mV s⁻¹) than that of ethyl group as can be seen from **Fig. S13**²³. So, considering reversibility, stability and higher $E_{1/2}$ value of the redox couple, (3) was chosen as the catholyte material for demonstrating an organic redox battery. The electrolyte containing 6 mM of (3) and 0.1 M TBAPF₆ as supporting electrolyte was deaerated by N₂ for 10 minutes to use as catholyte before starting the experiment. Anolyte solution containing 0.1 M TBAPF₆ was purged with O₂ for 10 minutes before starting the measurements. **Fig. 4(a)** and (b) shows the CV of redox couples O₂ / O₂⁻ and (3) / (3⁺) recorded at different scan rates for evaluating the diffusion coefficient of the respective redox species. The anodic peak current of (3) / (3⁺) and cathodic peak current of O₂ / O₂⁻⁻ redox couples were plotted against square root of scan rate ($\sqrt{\nu}$) as shown in **Fig. 5(a)** and (b) indicating diffusion controlled mass transfer of the redox active species.



Fig. 4(a) shows the CV of (3) and (b) of O_2 / TBAPF₆ in in the 4:1 solvent mixture of ACN and DCM at different scan rates.



Fig. 5 (a) The plot of peak current vs. (scan rate)^{1/2} for (3) and (b) $O_2/TBAPF_6$ in the 4:1 solvent mixture of ACN and DCM.

Redox kinetics

Redox kinetics of charge transfer reaction at the electrode-electrolyte interface can be determined based on Koutecky-Levich equation given by **{1**},

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_l}$$
 {1}

Where *i* is the total current, i_k is the kinetically controlled current and i_l is the limiting current.

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{0.62 \, n \, F \, A \, D^{2/3} \omega^{1/2} \mu^{-1/6} \, C_0}$$
^{{2}}

where F is faraday's constant (96485 C mol⁻¹), ω is rate of rotation (rad s⁻¹) of RDE and μ is kinematic viscosity (cm² s⁻¹) of ACN : DCM (4 : 1) medium from {2}.

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Fig. 6 (a) Polarisation plot for 2 mM of (3) in 0.1 M TBAPF_6 supporting electrolyte in the 4:1 solvent mixture of ACN and DCM at different rotation rate of RDE. (b) Koutecky-levich plot. (c) Tafel plot and (d) Levich plot

Fig. 6(a) shows the polarization plots for 2 mM of (3) at different rates of rotations. Fig. 6(b) shows linear relationship for the plot of i⁻¹ vs. $\omega^{-1/2}$ for a series of over-potentials ($\eta = E_{applied} - E_{onset}$) of 10 mV, 20 mV, 30 mV, 40 mV, 50 mV, 60 mV, 70 mV and 80 mV. Y-axis intercept at (ω)^{1/2} = 0 provides the $\frac{1}{i_k}$, from which i_k , corresponding to different potentials are calculated. A plot of *log* i_k against η provides the exchange current density value from the y-axis intercept at $\eta = 0$ (Fig. 6(c)). The kinetic rate constant is obtained from {3}.

$$i_0 = n F A k_0 C_0$$
 {3}

 where i_0 is the exchange current density (A cm⁻²). The value of k_0 is determined to be 1.12 × 10⁻³ cm s⁻¹. Using the RDE data, diffusion coefficient has been determined employing the Levich equation {4}. The estimated kinematic viscosity is 4.39 × 10⁻³ cm² s⁻¹. The diffusion coefficient determined using {4} is 1.8 × 10⁻⁵ cm² s⁻¹ which is comparable to the value reported using the CV studies (1.3 × 10⁻⁵ cm² s⁻¹).

 $i_l = 0.62 \text{ n F A D}^{\frac{2}{3}} \omega^{\frac{1}{2}} \text{ C v}^{\frac{1}{6}}$

{4}

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 $D = 1.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$

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Sl No	Molecule	Electrode	Electrolyte	Heterogeneous rate constant, k_{θ} (cm s ⁻¹)	Diffusion coefficient, D (cm ² s ⁻¹)	Reference
1	2,5-di-tert-butyl-1- methoxy-4- [2'methoxyethoxylbenzene	Glassy carbon	1 M LiTFSI in MeCN	0.9×10^{-2}	$7.3 - 8.2 \times 10^{-6}$	5
2	N 2,1,3-benzothiadiazole	Glassy carbon	1 M LiTFSI in MeCN	1.0×10^{-2}	1.5 -1.7 × 10 ⁻⁵	7
3	Benzophenone	Glassy carbon		1.32×10^{-2}	$1.01 - 1.62 \times 10^{-5}$	24
4	Benzoquinone	Glassy carbon	0.2 M Li ₂ SO ₄	2×10^{-3}	8.8 × 10 ⁻⁶	25
5	VO ₂ ⁺ / VO ²⁺	Graphite	1 M H ₂ SO ₄	3×10^{-7}	1.2×10^{-6}	26,27
6	V ³⁺ / V ²⁺	Graphite	1 M H ₂ SO ₄	4×10^{-3}	0.16 × 10 ⁻⁶	27,31
7	bis((3trimethylammonio)propyl)f	Glassy carbon	0.5 M NaCl	1.4 × 10 ⁻²	3.1 × 10 ⁻⁶	18
8	cī ,	Glassy carbon	0.5 M NaCl	2.2 × 10 ⁻²	3.3×10^{-6}	18
9	Br 3,6-dibromo-9-(p- tolyl)-9H-carbazole	Glassy carbon	0.1 M TBAPF ₆	1.12 × 10 ⁻³	1.8 × 10 ⁻⁵	This work

Table. 1 Heterogeneous rate constant and diffusion coefficient for redox active organic molecules.

 From **Table. 1**, the diffusion coefficient and heterogeneous rate constant values determined for the organic molecule (3) in this work are comparable with the values of organic molecules used as battery materials and better that the vanadium counterparts used in VRFB. Such high values of D and k_0 are ideal for fabricating good redox flow battery.

Reaction schemes

The reaction at the positive and negative electrodes along with cell reaction is given below.



Reaction at negative electrode



Reaction at positive electrode

Net cell Reaction



3.2. Charge discharge

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In this study, the O_2/O_2 -redox couple was used as analyte along with (3)/(3⁺) as the catholyte{5} {6}{7}. Earlier, our group has reported O_2/O_2 -redox couple for non-aqueous battery in N,Ndimethylformamide medium ^{20,29}. Fig. 7(a) shows the comparison CV of (3) with the dissolved O_2 . Both electrolytes show reversible nature of the electron transfer reaction.



Fig. 7(a) CV of 5 mM of (3) and O_2 /TBAPF₆ (b) galvanostatic charge-discharge carried out at 2.4 mA cm⁻² in the 4:1 solvent mixture of ACN and DCM.

From Fig. 7(a), an open circuit voltage of 2.34 V is expected, if we consider $E_{1/2}$ of (3) / (3⁺) and O_2/O_2^{-} . Fig. 7(b) shows galvanostatic charge-discharge of the cell carried out at 2.4 mA cm⁻² for 60 cycles with a charging cutoff voltage of 2.4 V. Fig. 7(b) also shows the charge-discharge curves of the cell without (3) in the catholyte. As can be seen, there is polarization both during charge and discharge indicating absence of any faradaic (charge transfer) reaction in the electrolyte devoid of (3). The discharge capacity of the cell containing (3) increased from 90 mAh L⁻¹ in the 1st cycle to 134 mAh L⁻¹ in the 40th cycle and stabilized around this value beyond 40th cycle. The trend of increasing discharge capacity can be due to accumulation of radicals (due to difference in the charge and discharge capacity). For 6 mM of (3), the volumetric capacity of the cell is 160 mAh L⁻¹. The cell reaches a maximum discharge capacity of 152 mAh L⁻¹ in the 56th cycle with a

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percentage utilization (ratio of experimental discharge capacity to theoretical discharge capacity) of the reactant and coulombic efficiency (CE) being 95% and 53 % respectively.



Charged cell

The cell charges to a higher capacity than the theoretical capacity with a voltage plateau beyond 2.3 V due to regeneration of (3) from (3⁺) upon its reaction with crossed-over O_2 {8}. Since a porous separator is used, the cross-over becomes inevitable. It is to be noted here that O_2 supply to the anolyte is unlimited due to continuous exposure to O_2 . In order to explore the stability of (3) in the presence of O_2 , the positive electrolyte was saturated with oxygen and 10 CV cycles were performed to capture the redox signature of the (3) at 50 mV s⁻¹ as shown in Fig. 8. Following this experiment the working electrode was held at -1.24 V for 5 minutes in order to produce superoxide in-situ. To study the reaction between superoxide and (3), a CV was recorded again to capture the redox signature of the reaction of superoxide with (3), the redox current of the (3) has reduced which probably indicates decomposition of the carbazole. To confirm the loss in redox activity is due to the reaction of superoxide with (3), the above sequence of experiment was repeated saturating with N₂ instead of O₂ and there was no change in the redox activity of (3).

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Fig. 8 CV of 1st and 10th cycles of **(3)** before and after chronoamperometry (CA) for 300 s with oxygen saturated electrolyte. **Inset** shows the CA plot for 300 s.

The cell suffers an irreversible capacity loss of 55 mAh L⁻¹ and 63 mAh L⁻¹ at 40th and 50th cycle numbers. Discharging the cell at 2.4 mA cm⁻² leads to considerable amount of polarization due to concentration polarization associated with low concentration of **(3)** and high ohmic drop of the electrolyte due to its poor conductivity. To identify the sluggish reaction, electrochemical impedance spectroscopy (Nyquist plot) of 5 mM solution of **(3)** and oxygen saturated ACN:DCM (V/V 4:1) solutions were recorded at 1.09 V and -1.24 V vs. Ag/Ag⁺, respectively as in **Fig. 9**.



Fig. 9 Nyquist plot of anolyte and catholyte along with fitted circuits in the inset.

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In the positive electrolyte, there is a semicircle corresponding to the charge transfer process occurring at high frequency region and a sloped straight line in the low frequency region corresponding to the diffusion of the (3). An equivalent circuit shown in **Table 2** is used to fit the Nyquist plot. A charge transfer resistance (R_{CT}) of 44 Ω was observed with a Warburg admittance (Y) value of 2.6 x 10⁻³ mho s^{1/2} correspond to the diffusion characteristics of (3). Y is related to Warburg impedance Z_W as shown in equation {9}, wherein $\omega \sim 0.16$ Hz.

$$Z_W = \frac{1}{Y_{\cdot}\omega^{1/2}}$$
^{{9}

Similar analysis performed at the negative electrolyte indicates presence of two semicircles, one probably corresponds to superoxide and the other correspond to the peroxide formation. R_{CT} of high frequency semicircle is 73.7 Ω and the mid frequency one is 252 Ω . Y of the dissolved oxygen species is 2.6 x 10⁻³ mho s^{1/2}. The solution resistance Rs was nearly same for both positive and negative electrolyte as they contain same supporting electrolyte. Comparing the R_{CT} values of the positive and negative electrolyte, O_2 / O_2^{-} redox couple seems to be limiting the performance of the battery.

Table 2 Shows the parameters of Nyquist plot for anolyte and catholyte.

Γ	Electrolyt	χ^2	$R_{S}\left(\Omega ight) /$	$R_{CT1}(\Omega)$	$Y_1(mho \times s^n)$	n ₁ /	R _{CT2}	Warburg, Y	$C_{2}(F) / %$
l	e		% Error	/ %	/ % Error	%	(Ω) / %	(mho×s ^{1/2}) /	Error
l				Error		Error	Error	% Error	
ŀ									
	Negative	7.6×10^{-4}	37.8/	73.74/	1.65× 10 ⁻⁵ /	0.87 /	252.6/	2.6×10^{-3}	1.3×10^{-7}
			1.9	2.15	12.8	2.2	2.28	3.5	3.15
L									
	Positive	3.3×10^{-4}	41.7/	44.3/1.2	-	-	-	3.2×10^{-3}	$2.3 \times 10^{-7}/3.0$
I			1.1					0.82	
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Fig. 10 compares the charge and discharge capacity of the cell with respect to cycle number and inset plot shows the coulombic efficiency of the cell measured at 2.4 mA cm⁻². In general there is a continuous increase in the discharge capacity of the cell as shown in **Fig. 10**. Enhancing the solubility of the analyte and conductivity of the non-aqueous medium is paramount in realizing battery with lesser overpotential and better performance. In order to improve the solubility, 3,6-dibromo-9-phenyl-9H-carbazole may be functionalized in the para position (which is not electrically in contact with the redox part of the carbazole) with methoxy and cyano functionality which have high affinity for solvents such as ACN, DCM hence improved specific capacity of the



Fig. 10 Capacity retention plot of the cell. Inset shows the coulombic efficiency with respect to cycle number.

electrolyte. Improving solubility by suitable structural modification of organic core will lead to enhancement in the capacity of the cell. Our aim in this work is to exemplify the working of carbazole derived catholyte material in a flow battery, for which we have chosen oxygen as the counter electrode material. The other materials which can be used in place of O_2 are 9-fluorenone, benzophenone and N-substituted phthalimides. Our future studies are in the above said directions. In addition, finding a suitable ion-conducting membrane would reduce the crossover of the active

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species, thereby limiting the charging capacity and extending the discharge capacity to theoretical capacity.

4. Conclusions

We have designed an organic molecule capable of showing reversible redox behaviour at higher potential thereby opening an avenue for better energy density of the battery. We have fabricated a cell using (3) and O₂/TBAPF₆ as the catholyte and anolyte, respectively in the solvent mixture of ACN : DCM (4 : 1). Labile positions of the carbazole core are suitably substituted to enhance the redox potential and show good reversible redox behavior. This combination of electrode materials offer an open circuit voltage of ~ 2.3 V. The diffusion coefficient and heterogeneous rate constant of 1.8×10^{-5} cm² s⁻¹ and 1.12×10^{-3} cm s⁻¹, respectively, for the (3), is on par with those already reported in the literature. We believe that the concentration of analyte and its diffusion will play vital role in bringing down the polarization rather than concentration of the supporting electrolyte at the current densities employed in this work. Hence, improving solubility of the analytes would be way forward to improvise this battery performance.

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