Naphthol bis-indole derivative as an anode material for aqueous rechargeable lithium ion battery

R. Anil Kumar2, R. Vijeth Shetty1,2, G. S.Suresh1*, K. M. Mahadevan2*

1Department of Chemistry and Research Centre, NMKRV College for Women, Jayanagar, Bangalore 560 011, Karnataka, India.
2Department of Studies and Research in Chemistry, Kuvempu University, PG-Centre, Kadur 577 548, Karnataka India.

*Corresponding author

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Abstract

Aqueous or non-aqueous rechargeable lithium ion batteries with organic electrodes as a current carrier can perform effectively sensible and affordable energy storage devices due to large accessibility of organic materials. Here we report a high-performance lithium-based energy storage device using 3,3′-(naphthalen-1-ylmethanediyl)bis(1H-indole) (NBI) as anode material for Aqueous Rechargeable Lithium-ion Battery. The active material is synthesized by condensation between indole and naphthaldehyde under stirring in glacial acetic acid, followed by lithiation by ball milling method. The obtained samples have been characterized by the combination of elemental analysis, NMR, FT-IR and powder XRD. The electrochemical measurements show that the cell Li-NBI | Sat. Li2SO4 | LiFePO4 has been delivered an initial discharge capacity of 113 mAh g\(^{-1}\) at lower current density. At the high current density 75 mAh g\(^{-1}\) discharge capacity can be achieved, which represents its high rate capability. Consequently, the as-prepared Li-NBI could be a potential active species as low cost anode materials for lithium batteries. The kinetics of electrode reactions under saturated Li2SO4 have been studied by Potentiostatic Electrochemical Impedance Spectroscopic method, show the semi-infinite behaviour at peak potentials. These considerations may be rendering the effective rate performance during charge/discharge process. Copyright © 2018 VBRI Press.

Keywords: Aqueous rechargeable lithium-ion battery, cyclic voltammetry, galvanostatic charge potential limit, potentiostatic electrochemical impedance spectroscopy.

Introduction

The raise in energy expenditure in many sectors is a direct indication of the cost-effective development of a country. The developing countries mainly required the energy sources for their efficient activities in all the sectors. However, the commercialization of energy production has been demanding due to the indefensible nature of non-renewable energy resources and environmental management. Therefore, developments of unconventional eco-friendly renewable energy sources have been widely investigated.

The storage of energy mainly focused on the designing of batteries and capacitors which should be easy to handle and fixed stores of electric power. Consequently, such technologies have been developed for lead acid, nickel–cadmium, nickel–metal hydride, lithium ion batteries etc.[1,2] Among which the rechargeable lithium ion batteries (LIBs) plays a major role in delivering high charge–discharge current rates for commercial applications [3]. Their development has been comprehensive to future developments in energy storage technologies with high power and high energy density for use in large scale applications.[4–6]

In the mid-1990s, a new type of rechargeable lithium-ion battery with an aqueous electrolyte was reported [7,8]. This battery uses lithium-intercalation inorganic compounds such as LiMn\(_2\)O\(_4\), LiNi\(_{0.8}\)Co\(_{0.2}\)O\(_2\), and VO\(_2\) as the electrode material and an alkaline or neutral aqueous electrolyte, and can overcome the disadvantages of non-aqueous lithium-ion batteries, such as high cost and safety problems [9–11]. Due to these aspects the large-scale development of energy storage systems has been restrictive. With respect to these aspects, Beck and Ruetschi [12] stressed their effort on the “Three E” criteria, specifically, energy, economics (reasonable manufacturing costs and long cycling performance), and environment (safe, non-toxic and high dependability), to develop an appropriate energy storage system to reach the present generation’s needs for applications. Thus, the use of aqueous electrolytes has been suggested as a capable move towards the aqueous battery system with low cost and high safety.
However, since its cycling was reported to be very poor it failed to attract strong interest from researchers. But to date, the ARLB electrochemical performance has been significantly enhanced with long cyclability and high rate capacity; these developments have rendered the interest of an increasing number of researchers towards the aqueous system.

The above consideration is based on electrolytes to be used in battery system; along with it the research sheds light on the progress of low cost safety electrode system to attain better results. The conventional rechargeable batteries with inorganic based electrodes work on redox reactions of metal ions in these. These electrodes improve the unsustainability, low yield, and environmental unfriendliness of metal elements. As a result, it is necessary to extend our view on the development of economically affordable and environment friendly organic electrode materials for rechargeable batteries [13].

Due to the above two significant criteria regarding aqueous electrolyte and organic working electrodes, the development of new battery system has taken an interesting path way in energy conservation stream. Although, the aqueous electrolyte has lesser output capacity due to the cell voltage, it is limited to the decomposition voltage of water (at about 1.3 V).

Keeping this in view, in the present studies, we have used a Naphthol derivative of bis-indole called 1-(di-1H-indol-3-ylmethyl) naphthalen-2-ol (NBI) as an organic electrode material for an aqueous rechargeable lithium battery. The Li-ions reduction processes are assisted by the presence of indole group with conjugated structure. The hyper conjugated system facilitates the localization of electrons and the –NH groups of bis-indole get involved in lithiation/delithiation process during electrode reaction. The synthesis of NBI and Li-NBI is carried out by conventional reflux process and ball milling methods respectively. The structural integrity towards the electrochemical processes is examined by both physical and electrochemical characterizations to prove their wide applications in the field of ARLIB technology.

The battery testing studies by Galvanostatic Charge Potential Limit reveals an appreciable discharge capacity of about 113 mA h g⁻¹ with1.2 V average potential by coupling with LiFePO₄ as a cathode [14]. From the impedance measurement it remarkably reveals that, the Li-NBI electrode’s effectiveness increase with the increase in charge transfer resistance during peak potentials. This deliberation may be rendering the useful rate performance during charge/discharge process.

**Experimental section**

**Materials and reagents**

The Analytical grade chemicals were used directly as received commercially. Melting point was determined in open capillary and is uncorrected. FTIR was recorded (400–4000 cm⁻¹) using KBr pellet method on Shimadzu-8400S spectrometer. 1H NMR was measured at 400 MHz using Bruker NMR spectrophotometer.

**Scheme of synthesis**

The synthesis of 1-(di-1H-indol-3-ylmethyl)naphthalen-2-ol is depicted in Scheme 1. 1-(di-1H-indol-3-ylmethyl)naphthalen-2-ol was obtained by condensation reaction between commercially available indole and 2-hydroxy-1-naphthaldehyde under stirring in glacial acetic acid as catalyst and solvent. The completion of the reaction was monitored by TLC (9:1 PE: EA). After the completion of the reaction, the reaction mixture was diluted with 20 ml of distilled water. The product separated out from the reaction mixture was filtered and washed with water; a pink colour crude product was obtained. The obtained crude product was purified by column chromatography using silica gel(60-120) as stationary phase and gradient of pet ether and ethyl acetate as mobile phase (9:1 v/v) to obtain the desired product 1-(di-1H-indol-3-ylmethyl)naphthalen-2-ol.

![Scheme 1: Synthesis of 1-(di-1H-indol-3-ylmethyl)naphthalene-2-ol.](image)

**Cathode material preparation**

The cathode material LiFePO₄ used in this study was synthesized by Reactions under Autogenic Pressure and at Elevated Temperature (RAPET) method [14]. As per the typical preparation procedure, the stoichiometric amounts of finely powdered and pelletized mixture of Li₂CO₃, Fe₃O₄·2H₂O and NH₄H₂PO₄ was heated at high temperature of about 700°C for 10 hrs in a tubular furnace. The crystallographic investigation done by X-ray powder diffractions (XRD) using AXRD Bench-Top Powder Diffraction System and obtained data was exactly matching with previously done work [14]. For the electrochemical investigations under aqueous media, Li₂SO₄ was used as electrolyte, which was procured from Sigma–Aldrich and used as received. A surface oxide free 2.23 cm² geometric stainless steel (SS) mesh current collector was used as the working electrode. A finely powdered mixture of stoichiometric amount in the ratio 80:10:10 of LiFePO₄, acetylene black and polytetrafluoroethylene (PTFE) stirred with few drops of N-methyl-2-pyrrolidone (NMP) were used to prepare electrode material slurry. The slurry coated electrode was subjected to heat treatment at 90°C for 12 hrs under vacuum.

**Construction of the cell for electrochemical performance**

The cell system Li-NBI | Sat. Li₂SO₄ | LiFePO₄ was immersed in sat.Li₂SO₄ electrolyte in a glass container. For three electrode systems, the Li-NBI was used as
working electrode with Pt foil and SCE as counter and reference electrodes respectively. The Cyclic voltammetry and electrochemical impedance spectroscopy studies were examined in a three electrode system, while for GCPL studies LiFePO₄ was used as the cathode.

Result and discussion

Spectral details

The reaction sequence used for synthesis of 1-(di-1H-indol-3-ylmethyl)naphthalen-2-ol (NBI) is described in Scheme-1. The NBI was synthesised by condensation reaction in glacial acetic acid medium using indole and 2-hydroxy-1-naphthaldehyde. The crude product was purified by recrystallization using methanol as a solvent to get 1-(di-1H-indol-3-ylmethyl)naphthalen-2-ol. The product was examined by spectral techniques such as IR and NMR to ensure the formation of reliable product. The IR spectral details from the (Fig.1a) reveals the appearance of a sharp peak at 3411 cm⁻¹ for N-H stretch and broadening of IR peaks after 3500 cm⁻¹ due to non-hydrogen bonded –OH stretch. At the vicinity of 3000cm⁻¹ renders the presence of aromatic – CH stretching frequency [15]. The NMR details are concluded as from (Fig.1b-d);¹H NMR (CDCl₃, 400 MHz) δ = 3.38 (s, Methane, C-H, 1H), 6.990 (s, Pyrazole, C-H, 2H), 7.148 (t, J= 8.4, Ar-H, 2H), 7.244 (t, J=7.2, Ar-H, 2H), 7.311 (s, J=7.6, Ar-H, 1H), 7.419 (d, J=2.4, Ar-H, 1H), 7.691 (d, J=18.4, Ar-H, 2H), 7.942 (N-H, 2H).

From the spectral data as predicted above, which reveals the NBI contains –NH group appears at 7.942 ppm chemical shift value render the presence of electronegative nitrogen atom [16]. The methane proton appears at 5.4 ppm and in the range 7.1 ppm to 7.6 ppm with two doublets and two triplets for aromatic protons. These observations prove the synthesised compound is of an indole derivative with high purity [16].

Electrochemical investigations

Prior to discussing the electrochemical aspects that appears in CVs for Li-NBI, the electroactivities of the electrode material in an aqueous electrolyte and its controlled potential window need to be recognized. This deliberation is necessarily done to know the evolutions of O₂ and H₂ gases during redox process [17]. In addition; the stability of electrode material in the electrolyte depends on dissolution factors, which fetch the redox peaks in cyclic voltammograms [18]. The typical cyclic voltammograms was run between 1.3 V and -1.0 V in saturated Li₂SO₄ aqueous electrolyte using Li-NBI mechanically immobilized stainless steel (SS) as working electrode and bare Pt electrode as counter electrode. From the (Fig. 2a) it is clear that the O₂ and H₂ evolution potentials are about1.2 V and -1.3 V, respectively, which reveals that the safe potential window to record the cyclic voltammogram in an aqueous medium is from -1.2 to 0.0 V which is within the disintegration potential of water [19]. Based on above factors to know the evolution potential of H₂ and O₂ in an aqueous saturated Li₂SO₄ electrolyte, we recorded the current/potential curves for bare electrode by linear sweep voltammetry as shown in (Fig. 3). It can be seen that the redox peak currents increases with increase in potential. The following equations show the H₂ and O₂ gas evolutions in an aqueous medium [20-21].

\[
2\text{H}_2\text{O} + 2\text{e}^-\rightarrow\text{H}_2 + 2\text{OH}^- ; E_0 (\text{pH}=7) = -0.65 \text{ V vs. SCE} \\
2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- ; E_0 (\text{pH} = 7) = +0.58 \text{ V vs. SCE} 
\]

(1)

(2)

i.e., the theoretically safe voltage limit is only 1.23 V. Similarly, in case of ZnS [21], Pb- and Bi-oxide electrodes show larger over potentials of about 2.7–3.0 V [22] in different aqueous electrolytes such as LiCl, NaCl, and H₂SO₄ [23, 24] etc. The reasons for such larger over-potential were explained by Jayalakshmi et al. [21]. Besides the O₂- and H₂-evolution peaks, there is a set of distinct and symmetrical redox peaks for Li-NBI working electrode. The manifestation of this pair of redox peaks can be described based on the redox activity of active site in Li-NBI molecule as shown in reaction Scheme 2, as it is identified that the active sites in the molecule take part in redox process.

Scheme 2. Electrode reaction mechanism of cathode at three electrode system under 0.5 mV/sec.

For this reason the anodic or oxidative peak accompanied by the de-lithiation, and the cathodic or reductive peak accompanied by the lithiation process. From the redox peak potential one can determine the
formal potential \( (E_f) \), by application of the Nernst law. According to this, the redox reactions must follow the activity of the lithium ion, \( \alpha_{Li^+} \), by depending on the \( E_i \).

\[
E_i = E^0 + 0.059 \log \alpha_{Li^+}
\]
i.e., the \( E_i \) is directly proportional to the logarithm of the concentration of \( Li^+ \) in electrolytic medium.

![Fig. 2. Cyclic Voltammogram](image)

The cyclic voltammograms of Li-NBI electrode with a scan rate of 0.5 mV s\(^{-1}\) in saturated \( Li_2SO_4 \) aqueous electrolyte as shown in (Fig. 2b-d). From the figure it shows that, a pair of redox peaks \( (E_{pa} = 0.66 \text{ V, } E_{pc} = 0.95 \text{ V}) \) with peak potential separation of 0.29 V. Herewith we could identify the cation involved in redox process of Li-NBI is \( Li^+ \) or not, we plot the results of \( E_i \) vs. \( \log [Li^+] \) as shown in (Fig. 2e). The formal potential is a mid-point between the redox peak potential of a voltammogram depicted as \( E_i = E_{pa} + E_{pc} / 2 \). As per theoretical concepts, this is assumed that the diffusion coefficients of the reactant and product are equal. From the figure, we can conclude that the well fitted straight line with a positive slope due to the redox peaks of Li-NBI in sat. \( Li_2SO_4 \), which attributed to the deinsertion/insertion process of lithium ion.

To examine the action of different scan rates on the redox activities of active material in \( Li_2SO_4 \) aqueous electrolyte, as shown in the (Fig. 2c), the CV curves at different scan rate regions like 0.1-1.0 mVs\(^{-1}\), were recorded. Even though the shape of the redox peak curve was approximately proportioned, the peak potential difference \( (E_{pa} - E_{pc}) \) among the two peaks amplified with increase in scan rates. This observation reveals the kinetics of electrode reaction on the scan rates.

As per theoretical perspective, at lower scan rates, the existence of reversible behavior is dominant, while at large scan rates, irreversible behavior is observable [24], which may predict that the electrochemical lithium-ion redox process alters from being kinetically quasi-reversible system to irreversible with increase in scan rates. For the present system as in figure one can clearly observe that, the appearance of reversible system with increase in scan rates with one pair of symmetrical redox peaks. From the figure, it is noticeable that both curves have the same form but the rise in scan rates influences the increase in total current. The magnitude of the voltammetric current of an electrode is enumerated by Randles–Sevcik equation. From the voltammogram it is evident that the electrochemical process undergoing a reversible charge transfer process depends on \( \Delta E_p \) and which is not depending on the applied scan rates but \( i_p \) increases with \( v^{1/2} \) and is directly related to the concentration of \( Li^+ \) ion in the electrolytic medium, which would take part in the redox process. This relationship becomes particularly important in the study of electrode mechanisms. However this electrochemical mechanism significantly depends on the ratio of \( i_{pa} \) to \( i_{pc} \), which should be close to one. In the reported electrode system, the \( i_{pa} \) to \( i_{pc} \) ratio is 0.85 \( \approx \) 1. To determine this practical factor, a scan rate study gives proper evidence. As per Randles–Sevcik equation, the peak current is directly proportional to the applied scan rate and a plot of \( i_p \) vs. \( v^{1/2} \) should be linear which is depicted in the (Fig. 2d). It is apparent that each voltammetric curve is the same but as increase in scan rates, the peaks current increases significantly. Here it is important to note that, at unchanged potential, the position of the current maximum occurs, which is a characteristic feature of electrode reactions that reveal fast electron transfer kinetics, usually termed reversible electron transfer reactions. This observation also holds well by considering the diffusion layer thickness and the duration of scan. By general observation of voltammograms at different scan rates, it is clear that, at lower scan rates it has taken a longer time to record. As a result, the diffusion layer thickness on the electrode surface will vary with the applied scan rates.

At a lower scan rate, the diffusion layer configuration is fairly additional from the beginning of the electrode reaction in differentiation to a fast scan. Accordingly the instability to the electrode surface is less important at slow scan rates than it is at faster rates. In view of the fact that, the electro activity of active material is depends on the output current. Therefore at lower scan rates the degree of the current will be negligible while it is prominent at high scan rates. Eventually an important point to note from the figure is that, at particular potential range the peaks show maximum current and this is a characteristic of Li-NBI electrode reactions with fast electron transfer kinetics. These kind of rapid electrochemical processes are often referred to as reversible electron transfer reactions.

(Fig. 2d) shows the association of peak currents and the square root of the scan rate \( (v^{1/2}) \), for the anodic and cathodic peaks respectively. The peak current is proportional to \( v^{1/2} \), which means that the electrode processes are diffusion-controlled [24]. By assumption, during electrochemical redox process the working electrode layer immobilized on the surface of SS disc is
considered as a compact uniform layer [25]. By the use of the following relationship between \( i_p \) and \( v^{1/2} \)
approximately one can determine the mean diffusion coefficient \( (D_{Li^+}) \) of \( Li^+ \) ions in the electrode active surface.

\[
i_p = (2.69 \times 10^{-5})n^{3/2}AD_{Li^+}^{1/2}v^{1/2}c_{Li^+}
\]

where \( i_p \) is peak current (A), \( v \) is scan rate (V s\(^{-1}\)), \( n \) is number of electrons per lithium ion \( (n = 1) \), \( c \) is lithium ion concentration and \( A \) is the actual surface area of electrode \( (cm^2) \). The geometric area of the electrode is 1 cm\(^2\). By using actual area of the electrode \( (A) \), one can determine the \( D_{Li^+} \). Subsequently, we can presume that the definite electrode area is equal to the sum of surface area of the coated active material. Theoretically, the larger value of \( D_{Li^+} \) is comprehensible, since the smaller particle sizes of the active material and the aqueous electrolyte render lower viscosity.

Taking into consideration the potential use of Li-NBI as an electrode in aqueous lithium ion batteries, an uninterrupted cyclic voltammogram as shown in (Fig. 2b) for active electrode in saturated Li\(_2\)SO\(_4\) aqueous electrolyte was carried out. For this electrode, the peak potentials remain approximately invariant and peak currents decline slightly with scanning. While peak currents decrease with cycling, the CV curves have distinct peaks and exceptional reproducibility. These characteristics illustrate the good reversibility and cycle life of Li-NBI as an anode material in aqueous lithium ion batteries.

A three electrode cell was assembled in a saturated Li\(_2\)SO\(_4\) aqueous electrolyte using Platinum foil as counter and SCE as reference electrode and Li-NBI supported on stainless steel mesh electrode \( (1 \text{ cm}^2 \text{ in diameter}) \) as the working electrode. Galvanostatic charge/discharge cycling of the cell was carried out at steady current rates of C/8 in the potential ranges of 1.0 V to -1.0 V as the potential window for CV. Both GCPL as well as CV experiments were carried out at room temperature using Five Channelled VSP Biologic Science Instruments running EC-LAB software.

**Galvanostatic charge discharge studies**

The battery testing process was carried out by GCPL method to have an ideal picture of the lithium redox performances and electrochemical mechanism of anode material. An electrochemical cell Li-NBI | Sat. Li\(_2\)SO\(_4\) | LiFePO\(_4\) was subjected for charge/discharge process. The obtained results of battery testing process are depicted in (Fig. 3a-d).

From (Fig. 3a) for the charge/discharge curves of cell at C/6 rate delivered 113 mA h g\(^{-1}\) in the voltage range of 1.2 V. From the figure it is clear that, the discharge/charge capacities in the first cycle of cell are roughly 113/118 mA h g\(^{-1}\) with coulomb efficiencies of approximately 96%. The GCPL studies up to 100 cycles are as depicted in (Fig. 3b). From the figure it is clear that in the first cycle, the appearance of a small plateau region in the range 0.1 to-0.3 V render an electrochemical lithiation of active site of the molecule, which agrees with the appearance of a cathodic peak in CV in the vicinity of -0.5 V. The electrode reactions are in aqueous medium is as predicted in Scheme 3.

From the second cycle onwards the disappearance of plateau represents that a complete electrochemical lithiation of active material occurred during the first cycle. This sort of irreversible reaction, in addition to this the configuration of solid electrolyte interface (SEI) on the anodes [26, 27], and pulverization of active species influences the discharge capacity fading from 113 to 76 mA h g\(^{-1}\) between 1\(^{st}\) to 100\(^{th}\) cycle respectively.

![Electrode Reaction](image)

**Scheme 3:** Overall electrode reaction of cell Li-NBI | saturated Li\(_2\)SO\(_4\) solution | LiFePO\(_4\)

![Galvanostatic charge potential limit studies](image)

**Fig. 3.** Galvanostatic charge potential limit studies of (a) Li-NBI | sat. Li\(_2\)SO\(_4\) | LiFePO\(_4\) cell first cycle at C/6 rate (b) multiple cycles at C/6 rate to show cyclizability (c) Coulombic efficiency up to 100 cycles (d) at different current densities to render the rate capability of the cell Li-NBI | sat. Li\(_2\)SO\(_4\) | LiFePO\(_4\).
capacities are 80/76 mA h g\(^{-1}\) and 63/31 mA h g\(^{-1}\), respectively. These results specify that the cell Li-N-BI | Sat. Li\(_2\)SO\(_4\) | LiFePO\(_4\) can exhibit better lithium storage capabilities with reversible reactions. From the figure it is clear that, the increase in current densities render the discharge capacity to decrease. This specifies that, the cell is quite suitable for an aqueous medium for huge current charge and discharge.

The effectiveness of the cell was monitored by the cycling performance and coulomb efficiency as rendered in (Fig. 3c). From the figure it is clear that, the coulomb efficiencies of the 100\(^{th}\) cycle at 0.05 mA current density are 68.18% but with an increase in current densities from 0.1 to 0.5 mA the coulomb efficiencies went above 95%. It must be noted that, the discharge capacity decreases suddenly from first to second cycle and then with increasing cycles of discharge decreases steadily with around 5% variations in successive cycles. This kind of fading in charge/discharge capacities is probably due to the change in the structure and functionalities of active species under electrochemical process. The capacity fading under applied current densities with time endorsed the pulverization of fresh active materials. These conditions lead to the changes in shape and structure of the molecules followed by change in their original properties too. Such in-situ newly formed active species through Li redox process, lead to failure of electrical connectivity among adjacent molecules [28]. In the early cycles, the pulverized species did not get in touch with each other, as a consequence, the capacity decreased. On the other hand, the active molecules began to get smaller and change their shape and structure when Li\(^{2+}\) were extracted. With continuous Li insertion/extraction process, the newly shaped molecules lose their structural properties may be due to electrochemical milling effects. Thus, the electrochemical transfer reaction of Li-NBI to NBI during cell reaction would be reversible to a definite point due to the very small structural modifications. The reversible charge/discharge process firmly specifies the particle size of the active species. According to Ahn et al. the decrease in the size of active species might reduce the activation energy for the reaction, thus enhancing the exchange reaction and produce the reversible capacity [29].

Potentiostatic electrochemical impedance spectroscopic studies

In order to investigate the kinetics of lithium insertion/extraction process, the three electrode system was subjected to PEIS over a frequency range of 100 kHz to 5 Hz under potential bias as shown in (Fig. 4 a-f).

The equivalent circuit for Nyquist plots at overall potential bias, which contains equivalent series resistance (R\(_{\text{e}}\)), SEI resistance (R\(_{\text{s}}\)), and charge transfer resistance (R\(_{\text{ct}}\)).

![Nyquist plot to show the impedance response of Li-NBI anode material at different charge and discharge potential bias (a) before oxidation, (b) during oxidation, (c) after oxidation and (d) before reduction, (e) during reduction, (f) after reduction process.](image)

The Nyquist plots of Li-NBI electrodes exhibit a semicircle in the high frequency region at -1.2 V during charging. A straight line in the low frequency range was observed. The high frequency semicircle is related to the boundary parameters such as surface film contribution, porous nature of the electrode and bulk properties [30, 31]. The low frequency straight line represents the Warburg impedance (Z\(_w\)) which indicates the diffusion process of Li ions in the electrolyte medium [32, 33]. Curves fitting in the Nyquist plots with the equivalent electrical circuit model are shown in (Fig. 4). The symbols R\(_s\), R\(_{\text{e}}\), R\(_{\text{ct}}\) and Z\(_w\), signify the solution resistance, contact resistance, charge-transfer resistance and Warburg impedance, respectively. It can be seen from Table 1 and Table 2 for the impedance spectral data, the R\(_s\) values of the electrodes are very low at high and low frequency region of Nyquist plots at oxidative and reductive peak potential.

| Frequency Range | R\(_s\) (|Ω|) | R\(_{\text{e}}\) (|Ω|) | R\(_{\text{ct}}\) (|Ω|) | Z\(_w\) (|Ω|) |
|-----------------|--------|--------|--------|--------|
| High Frequency  | 1      | 2      | 3      | 4      |
| Low Frequency   | 5      | 6      | 7      | 8      |

Table 1. PEIS parameters obtained by circuit fitting at charging potential bias.
With its lower $R_t$ value the Li-NBI organic based electrode established a better electrical conductivity. Compared to the EIS result of Li-NBI at oxidation and reduction potential bias are as shown in figure, the Nyquist plots before oxidation and reduction exhibits semicircle with a low $R_t$ value of 25.63 $\Omega$ and 81.60 $\Omega$ in the high and medium frequency range, indicative of the improved charge-transfer resistance of the electrode material. The EIS result of Li-NBI during oxidation and reduction render comparatively high charge transfer resistance than that of the results obtained after oxidation and reduction process at applied potentials. This considerable variation may be due to the presence of electro-active functionalities of organic molecule [34]. It is notable that the $R_{ct}$ of the Li-NBI during oxidative and reductive potentials are much larger than that of before and after peak potentials, which reveals that, the Li-NBI electrode efficiency increased with the increase in charge transfer resistance during peak potentials, These considerations may render be the effective electrochemical performance after charge/discharge process. The above factors also imply that the electroactivity of Li-NBI based on its structural manifestations significantly effects on the progress of the electrochemical reaction among the electrolyte and active materials, causing improvement in the electrochemical properties. The Nyquist plots at all potentials except early charge and discharge regions show 45° inclined lines at low frequency region. In this frequency region the spectrum reveals an apparent semi-infinite diffusion element due to the SS current collector interface, which blocks the diffusion of Li ions. These straight lines referred to as Warburg lines. The lithium ion diffusion coefficient ($D_{Li}$) was calculated from the plots in the low-frequency region. The following equations express the $D_{Li}$ values by EIS [33, 35, 36].

\[
D_{Li} = \frac{(RT)^2}{2(An^2F^2Cl_i\sigma)^2}
\]

\[
Z' = R_b + R_{ct} + \sigma \omega^{-0.5}
\]

where $R$ is the gas constant, $T$ is the absolute temperature, $n$ refers to the number of electrons involved per molecule during oxidation, $F$ is Faraday’s constant, $C_{li}$ is the concentration of lithium ions, $\omega$ is the angular frequency, and $\sigma$ is the Warburg factor, which has a relationship with $Z'$.

**Conclusion**

A new and an effective indole derivative 1-(di-1H-indol-3-ylmethyl)naphthalene-2-ol was synthesised by conventional method. The chemical structure was analyzed with the help of FT-IR and $^1$H NMR spectra. The electrochemical stability of the active material was checked by thermal analysis, which indicated that the thermal stability of Li-NBI in aqueous electrolyte. This derivative is one of the reliable eco-friendly anode materials with an appreciable discharge capacity and good electrochemical stability. The reversible electrochemical processes of electrode material were studied in an aqueous system of saturated LiSO$_4$ by using three electrode cell systems. The cell Li-NBI | sat. Li$_2$SO$_4$ | LiFePO$_4$ rendered significant electrochemical performance, which may take part promise able role in the field of rechargeable lithium ion batteries. The cell delivered an average voltage of 1.2 V and 113 mA h g$^{-1}$ discharge capacity with 96% coulometric efficiency. The electrochemical kinetics of electrode by impedance spectral studies provided the information about a better electrical conductivity by lower $R_t$ values and also predicted the improved charge-transfer resistance at peak potential bias. These notable electrochemical behaviours of the cell are clearly inferred on the basis of electrochemical studies. All these properties showed that the alternative for high-cost inorganic materials by organic moieties for RLIB have promising potential as a whole with electron-transporting material in organic electrochemical devices. We are currently applying these organic electrode materials as an anode material for aqueous rechargeable lithium ion battery. Thus, these results provide the significant route for the application of the Indole derivatives in energy storage devices.

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