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Organic materials as Electrodes for Li-ion Batteries

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14. ABSTRACT

The project studied organic electrode materials for rechargeable lithium batteries. Several organic compounds were synthesized, characterized and tested in battery configurations. The details are given for each class of materials. Various macrocycles, their synthesis, characterization and subsequent use in lithium-ion batteries were attempted. Ellagic acid, alizarin and phthalocycnines are relatively novel as organic electrodes in rechargeable lithium batteries, and ellagic acid and AS dye are found to be very promising, with high thermal stability. Use of these materials with magnesium- and zinc-based batteries is expected to be promising and further study is underway. Density functional theory (DFT) calculations are also being carried out to understand the structure-property relationship.

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Report on the work carried out on
‘Organic electrode materials for rechargeable lithium batteries’
(June 2013 – May 2015)

Project no.	AOARD 134015
Title:	Organic Materials as Electrodes for Li-ion Batteries
Institution:	Indian Institute of Science, Bangalore, India

Introduction

The project envisages the study of organic electrode materials for rechargeable lithium batteries. Towards this direction, several organic compounds have been synthesized, characterized and tested in battery configurations. The details are given below for each class of materials.Various macrocycles, their synthesis, characterization and subsequent use in lithium-ion batteries have been attempted to.

Lithium-based batteries are at the forefront of battery technology and research towards finding new materials to improve the performance are underway. Conductive organic polymers have been proposed as electrode materials as early as in 1980s. Since then, several organic compounds have been investigated for their potential use in Li-ion batteries. Many of the organic compounds are limited by their thermal stability, rate capability, cycle life and low energy density values. It has been recognized that molecules with hydroxyl and carbonyl groups in conjugation with aromatic systems may be efficient organic electrodes.

Results and Discussion

a. ***Ellagic acid - based compounds (this part of the work has already been given in the first year report).***

Extraction and characterization of ellagic acid: Pomegranate husk powder was used in the extraction of ellagic acid based on a reported procedure. In brief, tannin from finely ground pomegranate husk was extracted thrice using 60% ethanol in water, followed by acid hydrolysis in 5.0 % H_2SO_4 for 5 h and recrystallization from hot pyridine to obtain 99% pure crystalline, ellagic acid (EA). The structure is given in the NMR spectrum. Various techniques such as NMR, IR, XRD, SEM and thermal analysis have been carried out to characterize the material.

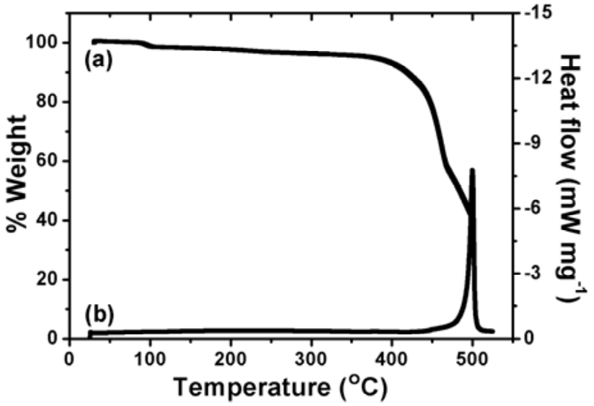


Figure 1: (a) Thermo gravimetric (TG) and (b) differential scanning calorimetric traces of EA at heating rate at 10 ^{0}C per minute under N_2 atmosphere.

It is noticed that the thermal stability of ellagic acid very good without any loss in weight up to 400 C as observed in the above thermogram.

The material was also characterized using NMR techniques and the data are given below.

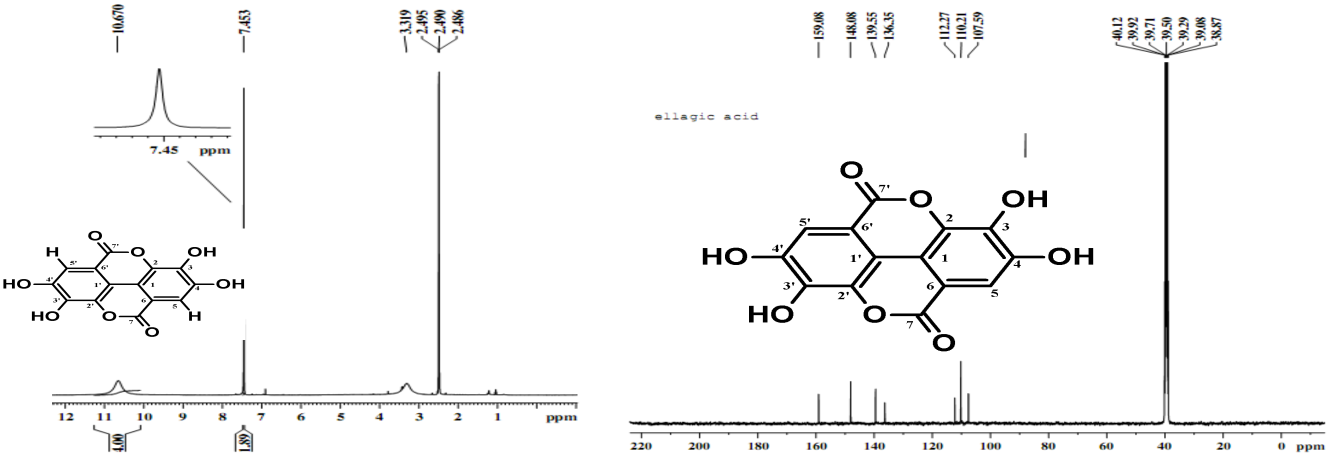


Figure 2: ^{1}H and ^{13}C NMR spectra of ellagic acid, solvent used was DMSO-d6.

^{1}H-NMR (DMSO-d_6) ppm: δ 7.45 (s, 2H, ArH), 10.67 (s, 4H, -OH), ^{13}C-NMR (DMSO-d_6) ppm: δ 159.08 (C7), 148.08 (C4), 139.55 (C3), 136.35 (C2), 112.27 (C1), 110.21 (C5), 107.59 (C6)

Electrochemical characterization and battery characteristics

Swagelok-type cells were used to follow the electrochemical performance with lithium metal electrode and separator (whatman GF/D borosilicate glass fiber sheet) soaked with 1M $LiPF_6$ in ethylene carbonate and dimethyl carbonate (1:1 in volume ratio) as the electrolyte. The cells were cycled between 0.5 and 3.3 V vs. Li/Li^+ and all capacities are reported in mAh with respect to the mass of EA.

Reversible lithiation and delithiation process is revealed in the voltammograms scanned between 3.5 and 0.5 V (Figure 3). The first cathodic scan shows large currents around 0.65 V which decrease and stabilize at positive potentials (~ 0.80 V) in subsequent cycles. Further cycling shows similar voltammograms with almost constant currents at all potentials. The first large peak around 0.65 V corresponds to lithiation of EA molecule along with the formation of solid electrolyte interface (SEI). As observed in the voltammograms between 3.5 and 0.5 V, lithiation / delithiation process occurs in two steps, the first one around 2.8 V and the second one at ~ 0.80 V. During the anodic scan, peaks observed around 2.3 and 2.9 V are associated with de-lithiation process. However, when cycling is carried out between 3.5 V and 0.05 V, Li ion intercalation / deintercalation processes associated with carbon support material are also revealed, as high currents around 0.25 V in the cathodic scan and a broad peak at ~ 1.1 V in the anodic scan. This is also confirmed by carrying out comparative studies using only carbon as well as carbon with EA as electrodes. It has been pointed out that conjugated carbonyl groups including quinones possess redox potentials below 3.0 V vs. Li/Li^+ and generally behave as cathodes. EA falls in this category as well. The open circuit voltage (OCP) observed is 2.8 V in the present studies.

Galvanostatic charge-discharge studies performed between 3.3 and 0.5 V (Fig. 3c) at a rate of one Li for 10 h. (C/10 rate) shows a first discharge initial drop observed from OCP of 2.80 V to 1.85 V followed by a plateau between 1.85 to 1.25 V and two irregular plateau around 1.25 - 0.75 V and 0.75 - 0.5 V with a discharge capacity of 740 mAh/g. The capacity obtained during first discharge is higher than the expected capacity for EA (maximum of 6 Li results in a theoretical capacity of ~530 mAh/g). The high discharge capacity is likely to be due to formation of SEI along with lithiation of EA. Upon charging, de-lithiation occurs in two regions. Subsequent cycles show capacity around ~ 450 mAh/g. The capacity loss and difference in the potential regions of the initial cycles are due to reactions of EA electrode and the electrolyte along with the formation of SEI. But, the capacity loss from second cycle to subsequent cycles is very small and ~75 % of the stable capacity is observed after several cycles. Fig. 3d shows the capacity versus number of cycles and the stability is observed to be very good. Individual capacities contributed by carbon (acetylene black, AB) and EA have been experimentally found out and it is observed that ~50 mAh [for the mass of AB used] capacity arises from AB and the rest is from EA which is around 400 mAh, that is equal to 4.5 Li ions per EA molecule.

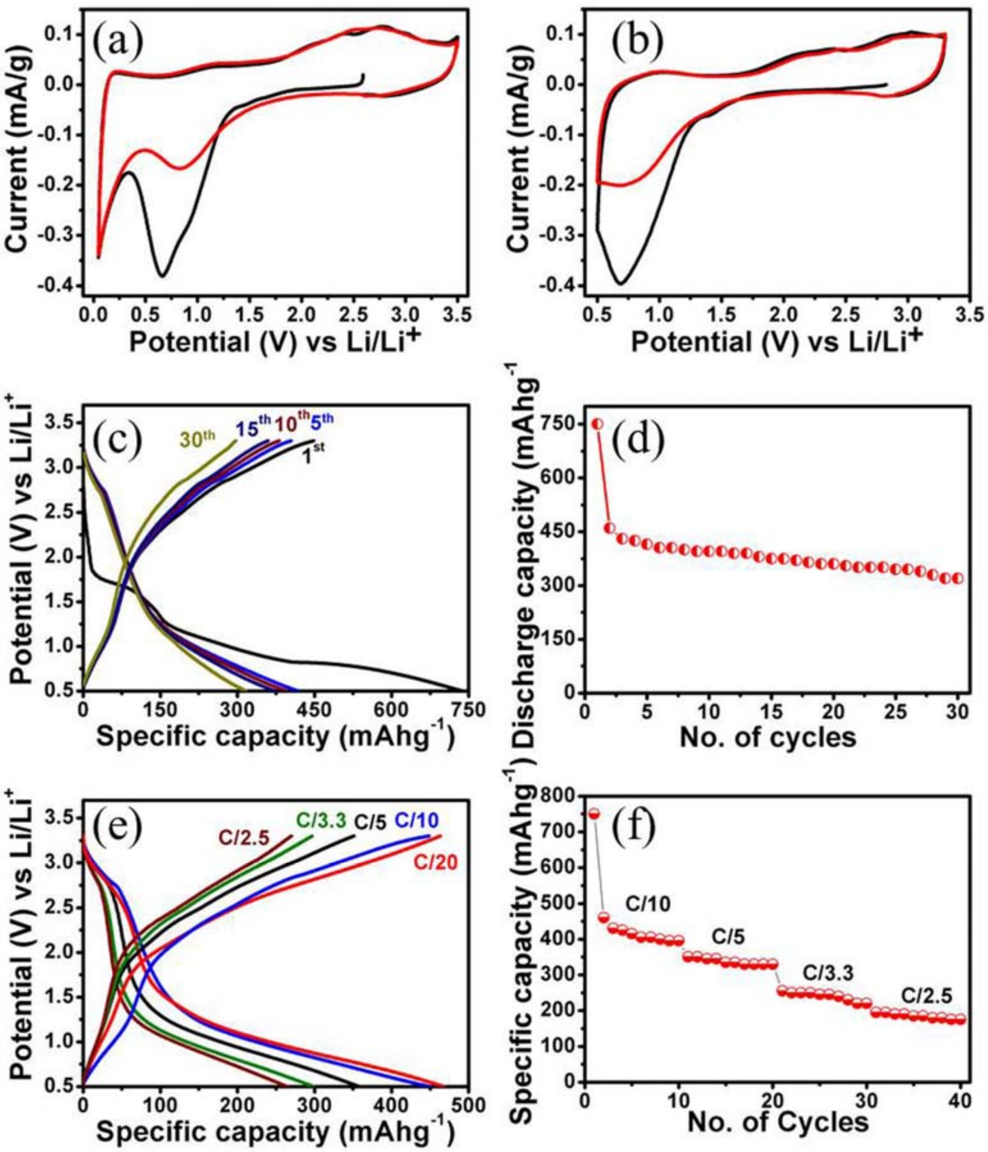
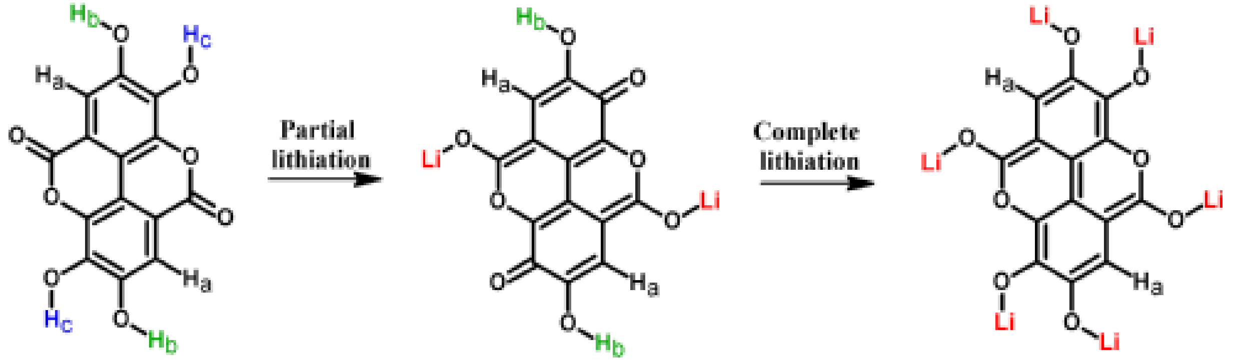


Figure 3: Cyclic voltmmograms of EA (at a scan rate 0.05 mVs^{-1}) (a) between 3.5 and 0.05 V and (b) between 3.3 and 0.5 V. (c) represents galvanostatic charge-discharge curves at C/10 rate for various cycles (1st to 30th cycle) and (d) indicates capacity variation with cycle number. (e) represents charge-discharge data at various rates and (f) represents variation of specific capacity with number of cycles at different discharge rates. Figure (d) is obtained from figure (c) and figure (f) is obtained from figure (e).

The rate capability of EA-based batteries has been followed at C/20, C/10, C/5, C/3.3 and C/2.5 discharge rates and the results are shown in Fig. 3e. The discharge curves at different rates show similar profiles and the stable capacity obtained at C/2.5 rate is 200 mAh/g. The capacities at different rates are found to be very stable as well (Fig. 3f). In the present studies, the cyclability and the capacity retention from 2nd cycle onwards point to the fact that the possibility of formation of LiF type species is low though the pKa1 of EA is 6.3 in aqueous solution, which is slightly acidic in nature. The solvents used are completely dry and free from moisture. The availability of protons in the electrolyte is very negligible which rules out any possibility of pseudocapacitive processes.

In order to investigate lithium reversibility into EA and possible mechanism of lithiation/de-lithiation process, *ex-situ* NMR spectroscopy has been carried out. Briefly, three separate swagelok cells are fabricated with EA as the working electrode and electrochemical measurements are carried out at C/10 rate. The charge-discharge measurements are terminated at three different potentials, and the EA electrode material removed from the current collector followed by centrifuging in organic carbonate solvent and subsequently dried under vacuum. The samples for NMR are prepared in glove box under argon atmosphere using DMSO-d6 as the solvent. The NMR spectra of three different samples discharged to 1 V and 0.5 V and charged to 3.3 V vs. Li/Li^+ are compared with pure or non-lithiated EA (Fig. 4). The non-lithiated EA exhibit a singlet at δ 7.45 ppm for two aromatic ring protons (H_a) and a broad singlet for four phenolic hydroxyl groups (H_b and H_c) at δ 10.67 ppm. Partially lithiated EA obtained by discharging to 1 V exhibit up field shift of two ring protons (H_a) to δ 6.99 ppm and that of phenolic hydroxyl groups (OH_b) is observed at δ 8.54 ppm. On the other hand, the NMR spectrum of completely lithiated EA, acquired at 0.5 V shows evidence for only two ring protons, H_a, at δ 7.24 ppm indicating lithiation of all four hydroxyl groups in addition to the lactones. Further, when fully charged to 3.3 V, the de-lithiated EA demonstrates the presence of ring protons (H_a) at δ 7.00 ppm and partly protonated phenolic hydroxyl groups at δ 8.49 ppm. This spectrum is similar to the one obtained at 1 V. The appearance of phenolic hydroxyl groups indicates de-lithiation of EA, but the obtained NMR spectrum is not identical to unlithiated or pure EA. However, it is confirmed that the lithiation/de-lithiation process of EA molecule is reversible. The probable mechanism during charge – discharge process may be given as follows.



Scheme 1: Possible electrochemical lithiation/de-lithiation process in EA molecule

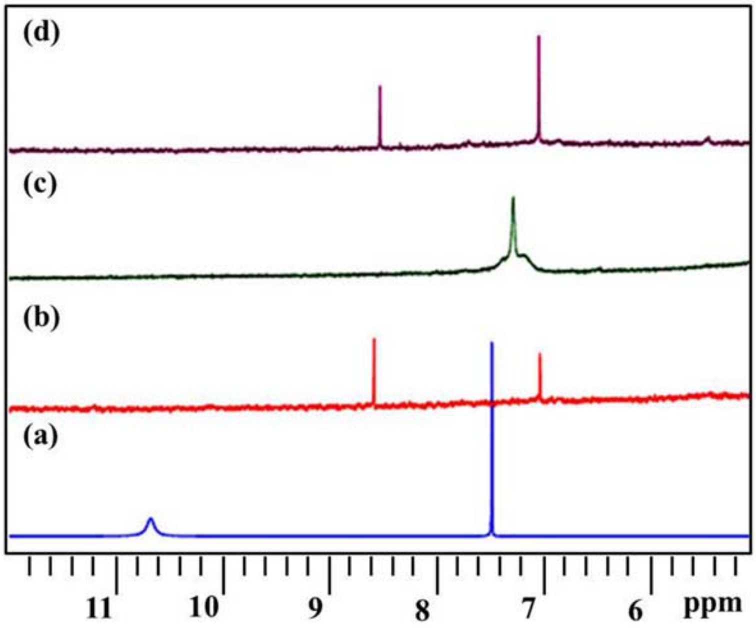


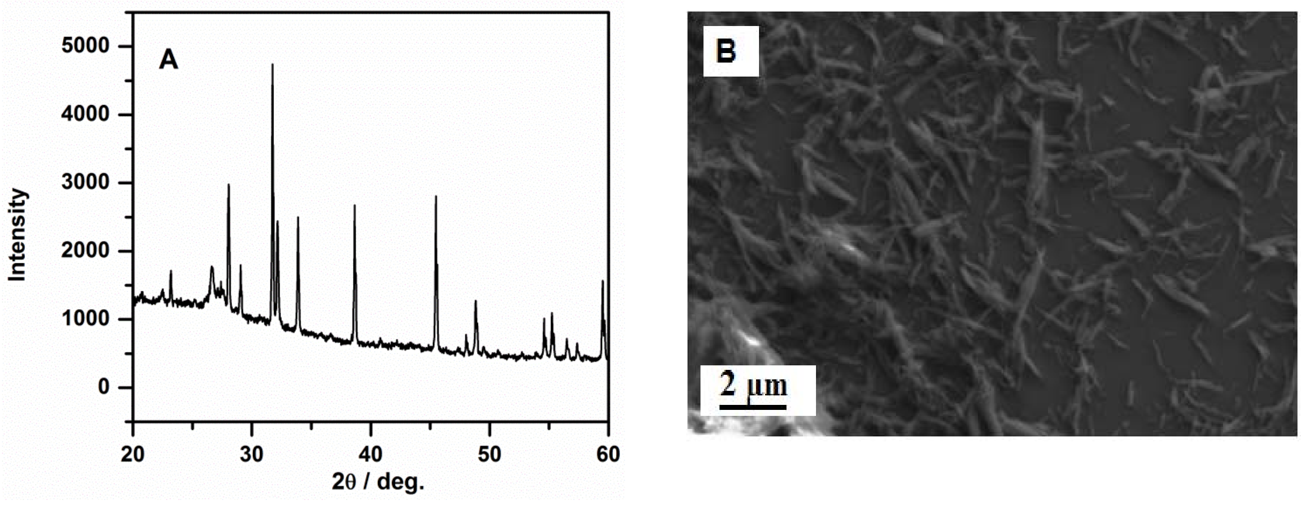
Figure 4: Expanded ^{1}H-NMR spectrum collected in DMSO-d6 at 400 MHz. (a) Pristine EA; Lithiated EA where the cell was discharged from open circuit voltage (b) to 1.0 V and (c) to 0.5 V. (d) represents de-lithiated EA electrode material where the cell was first discharged to 0.5 V and recharged to 3.3 V.

b. ***Alizarin dye - based electrodes***

Recently, it has been reported that a water soluble indigo carmine conjugated carbonyl organic dye can be used for storing reversibly, both lithium and sodium ions for rechargeable battery applications. In the present study, we have used a water soluble alizarin safirol conjugated carbonyl organic dye (AS) which can undergo four electron transfer redox process to accommodate four lithium ions per molecule. Hence, alizarin safirol dye is expected to exhibit high energy density. Furthermore, it contains polar sulphonate group, which prevents dissolution in propylene carbonate/ethylene carbonate electrolyte as a result high cycliability can be obtained.

Charge/discharge cycles at different current densities with a cut-off voltage of 0.5 V vs. Li/Li^+ for discharge and 3.0 V vs. Li/Li^+ for charging is employed. Cyclic voltammetry experiments are carried out using Bio-Logic work station, AS dye is used as working and lithium metal as counter and reference electrode respectively. The anode and cathode are separated by 1 M $LiFePO_4$ in ethylene carbonate and dimethyl carbonate electrolyte soaked glass micro fiber separator. H^1 NMR spectra are recorded on a Bruker DRX-300 and 400 MHz NMR spectrometer FTIR studies are carried out using PerkinElmer Spectrum one FT-IR spectrometer.

AS dye has been subjected to physical characterization techniques such as powder XRD, SEM and TGA analysis before lithiation/delithiation process. XRD pattern of AS dye (Figure 5A) depicts that it is in crystalline form which is further confirmed by SEM image as shown in Figure 5B. The weight loss of about 3 % before 100^{o}C in the thermogravimetric curve (Figure 5C) is due to the evaporation of absorbed water molecule. AS dye shows thermal stability up to 340^{o}C.



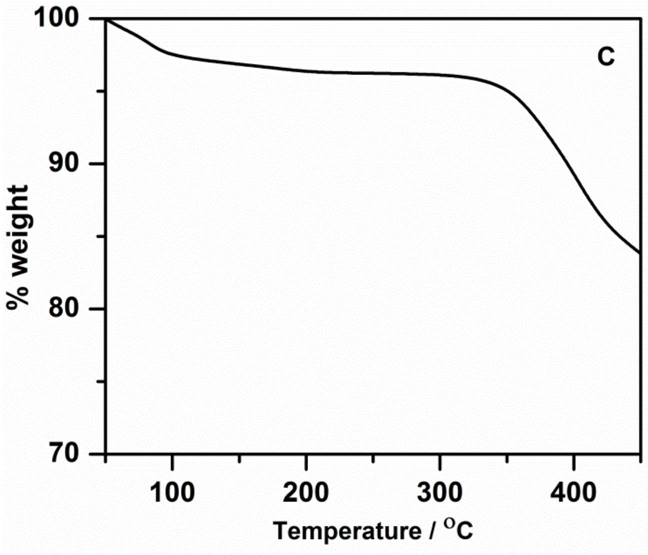


Figure 5: (a) Powder X-ray diffraction, (b) scanning electron miocrograph and (c) thermogravimetric data obtained on as-received alizarin (AS) dye.

Electrochemical properties of AS dye

Figure 6 shows the cyclic voltammograms of AS in 1 M solution of $LiPF_6$ dissolved in 1:1 mixture of ethylene carbonate (EC) and dimethay carbonate (DMC) at a scan rate of 0.01 Vs^{-1}. From the figure, it is confirmed that, first cycle appears quiet different from the subsequent cycles, i.e. two reduction peaks at 2.19 and 1.08 V and three oxidation peaks at 0.96, 2.06 and 2.16 V are observed that correspond to lithiation/delithiation process. The peak observed at 1.08 V in the negative scan is due to the formation of solid electrode interface (SEI). The cathodic peaks at 0.59, 1.4 and 2.2 V correspond to lithiation process. The peaks at ca. 0.96, 2.06 and 2.6 V are due to delithiation. Thus, from the cyclic voltammetric technique, it is confirmed that AS undergoes multiple steps to lithiation and delithiation.

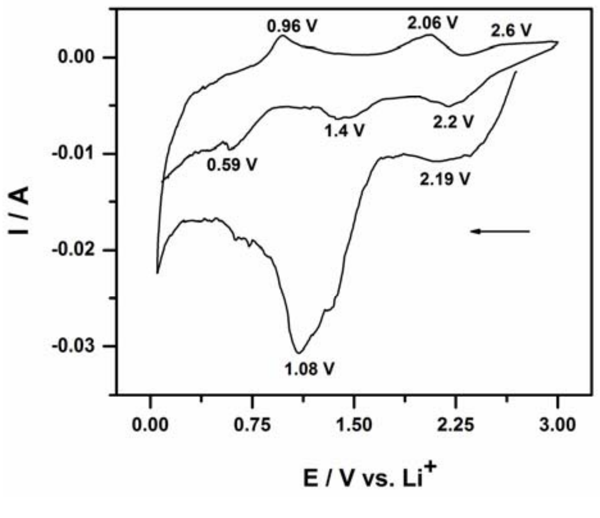


Figure 6: Cyclic voltammogram of AS dye in the potential window ranging from 3.0 to 0. 1 V at a scan rate of 0.01 Vs^{-1}.

Galvanostatic charge/discharge and impedance spectroscopy behavior of AS dye

The battery performance of AS dye is evaluated by using a half cell with a lithium metal. Figure 7a shows the charge/discharge profiles of AS dye electrode in the voltage window of 3 to 0.5 V at 1C rate. The first discharge curve shows a sudden voltage drop from 2.5 to 2 V followed by a plateau at ca. 1.9V with a high discharge capacity of 395 $mAhg^{-1}$. The theoretical discharge capacity of AS dye is found to be 288 $mAhg^{-1}$ (based on four electron transfer per molecule). The excess discharge capacity is attributed to an irreversible electrolyte decomposition reaction to form solid electrolyte interface. The AS dye is found to retain more than 70 % capacity after the completion of 100 cycles.

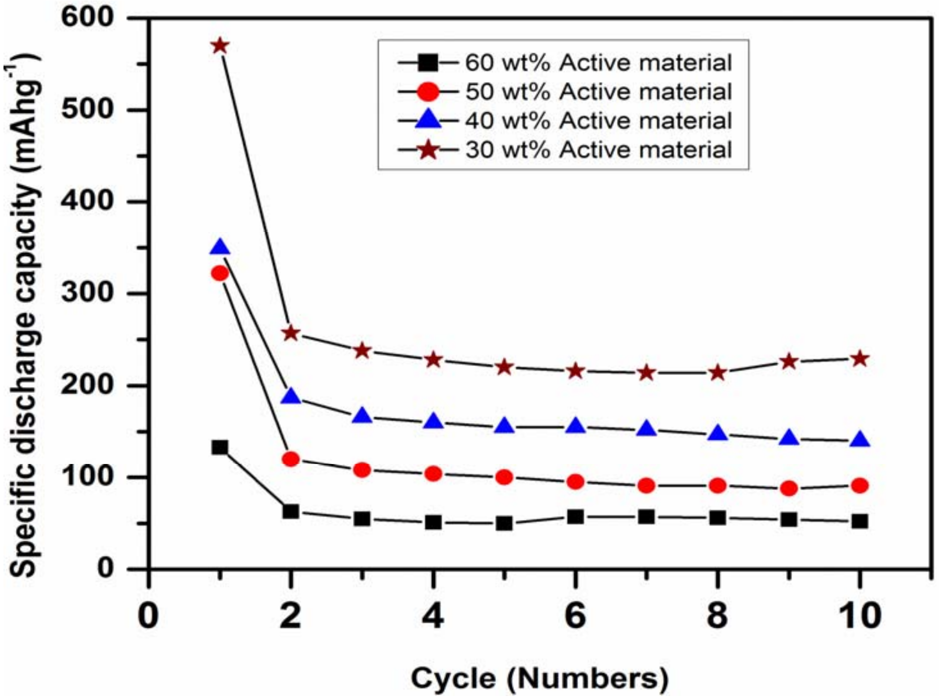


Figure 7: Specific discharge capacity as function of different weight percent of AS dye used for making the elctrodes.

Further, galvanostatic charge/discharge experiments conducted at various discharge currents (C/4, C/2, 1C and 2C) to investigate the rate capability of the AS dye electrode is shown figure 8. The shape of the voltage vs. specific capacity curves at higher current rate (2C) is similar to that of curves which obtained at lower current rate (C/4). Thus, high rate capability is demonstrated using this organic electrode material.

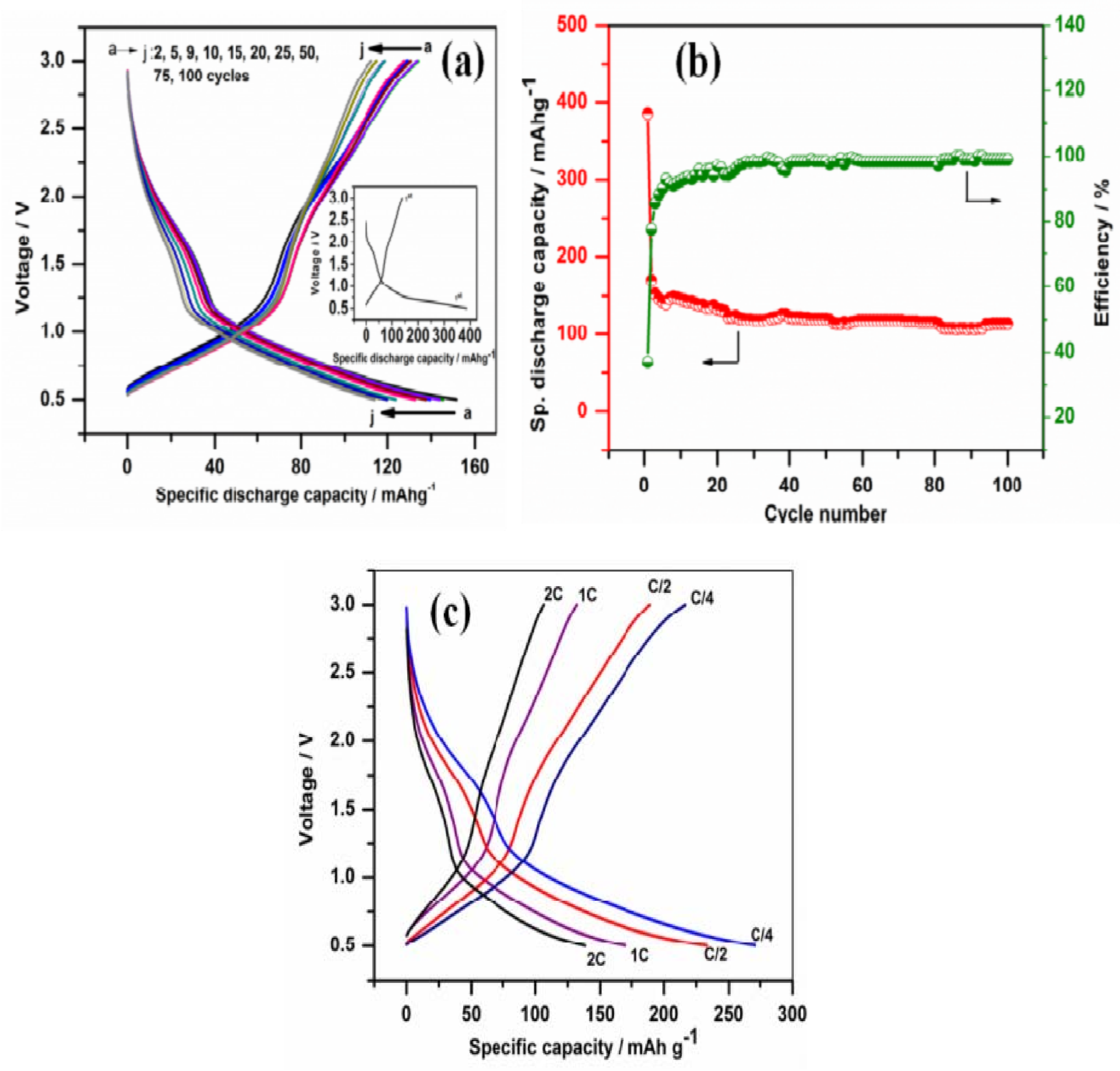


Figure 8: The electrochemical performance of AS dye a) voltage profiles, b) cyclability and Columbic efficiency, and c) rate capability.

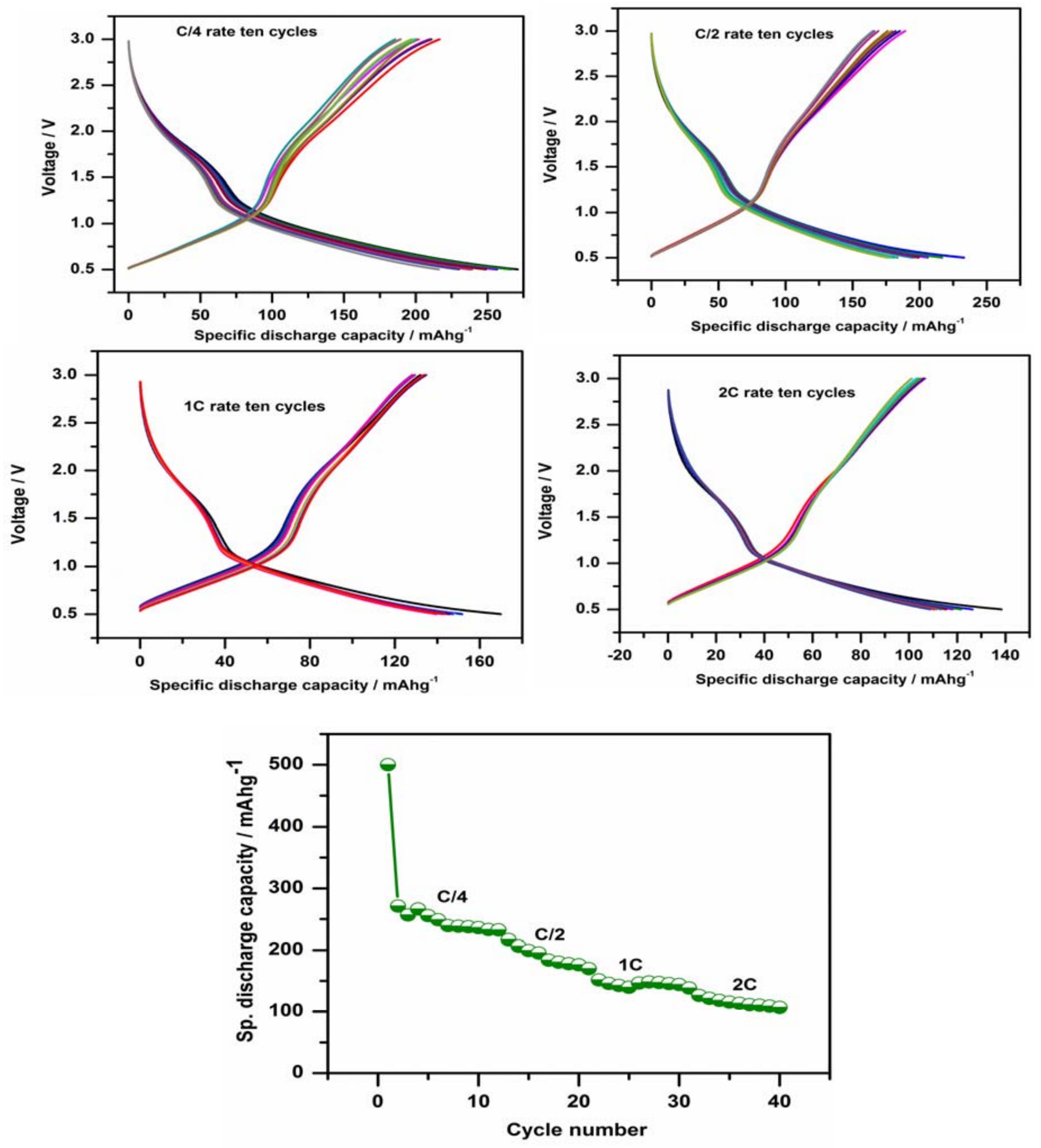


Figure 9: Voltage vs. specific capacity curves of AS dye at different current densities.

AC impedance spectra of AS dye electrode before lithiation and delithiation show high charge transfter resistnace (R_{ct}) of 1107 Ωcm^2 (Fig.10A) on the other hand after 75 cyles of discharging and charge process the R_{ct} decreases sygnificantly and reaches 99 Ωcm^2. This peculiar behaviour could be due to the stepwise lithiation/delithiation process leading to effective decrease in impedance of organic electrode. The equivalent circuit shown in figure 10B is used to simulate the experimentally obtained impedance spectra. Various elements used in the equivalnet circuit are solution resistance (R_s), charge transfter resistnace (R_{ct}), constant phase element (CPE) which is due to double layer cpacitance (C_{dl}), Warburg diffusion element (Z_w) and C_f and R_f in parallel are due to surface passivation on electrode surface.

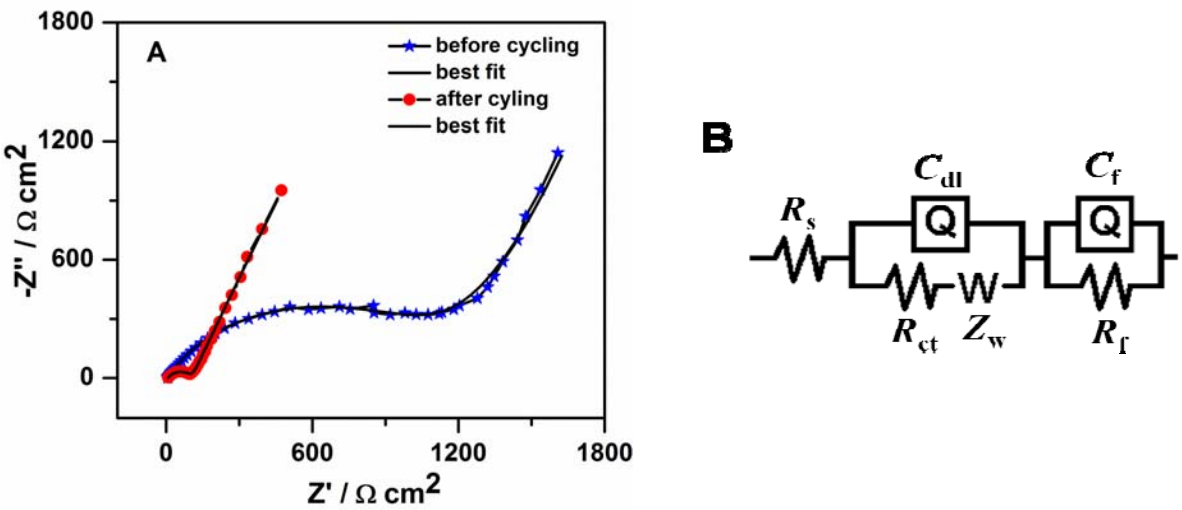
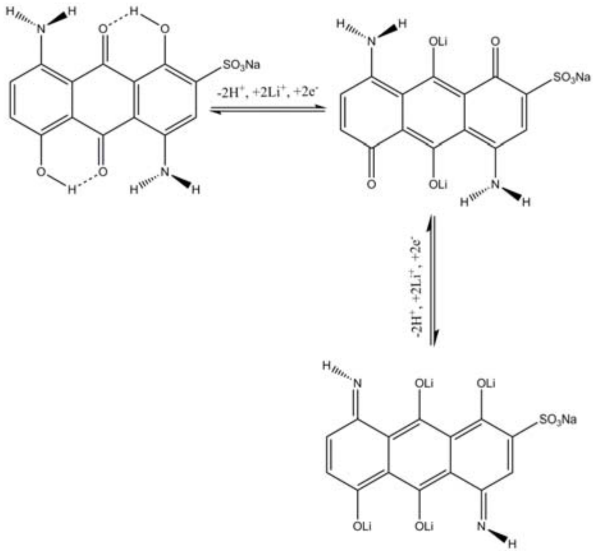


Figure 10: AC impedance spectra of AS dye before lithiation and after lithiation process. B. Equivalent circuit used for the simulation of experimental impedance spectra

Determination of lithiation/delithiation mechanism using NMR spectroscopy

In order to investigate lithium reversibility in alizarin safirol dye and to deduce the plausible reaction mechanism of the lithiation and delithiation process, ex situ NMR spectroscopy is carried out with AS dye in its complete discharged or charged state. To evaluate lithiation, discharge studies are carried out in the voltage window from 3 to 0.5 V at a C/10 rate. After completion of discharge step, the cell is transferred into the glove box and dismantled. The AS dye working electrode is washed with ethylene dicarbonate solvent to get rid of SEI and then dried at argon atmosphere. Finally, the lithiated AS dye is dissolved in DMSO-d_6 solvent and subjected to NMR studies. Similarly, the above mentioned procedure is followed for the charging process which is carried out form 0.5 to 3.0 V to obtain the corresponding NMR spectrum of delithiation. The obtained NMR spectra of delithiated and lithiated along with pristine alizarin safirol dye are given in Figure 11. ^{1}H NMR of pristine AS showed multiplet at δ 7.2 ppm for the ring protons, singlet at δ 7.75 ppm for the proton which is adjacent to polar sulphonate group, other singlets at δ 14.1, δ 14.75 ppm are assigned to hydroxyl groups and broad singlet at δ 8.15 ppm is assigned for two amine groups. In lithiated NMR spectrum, peaks corresponding to hydroxyl groups at δ 14.1, δ 14.75 ppm and amine group at δ 8.15 ppm are absent. This depicts the involvement of both hydroxyl and amine groups in lithiation process. Thus, AS dye undergoes four electron reduction reaction to form the compound which is given in the reaction scheme 2. The given structure is well agreement with obtained lithiated NMR spectrum. i.e., two doublets at δ 8.0 and δ 7.8 ppm assigned to two –CH aromatic ring protons, singlet at δ 7.5 ppm for the ring proton which is adjacent to polar sulphonate group and two multiplets at δ 7.3 and δ 7.4 ppm due to the formation of solid electrolyte interface formed during lithiation process. Similarly, delithiated NMR spectrum is almost similar to that of pristine AS dye except some additional peaks that could be due to solvent decomposition during the course of charging.



Scheme 2: Plausible lithiation/delithiation reaction mechanism in the AS system.

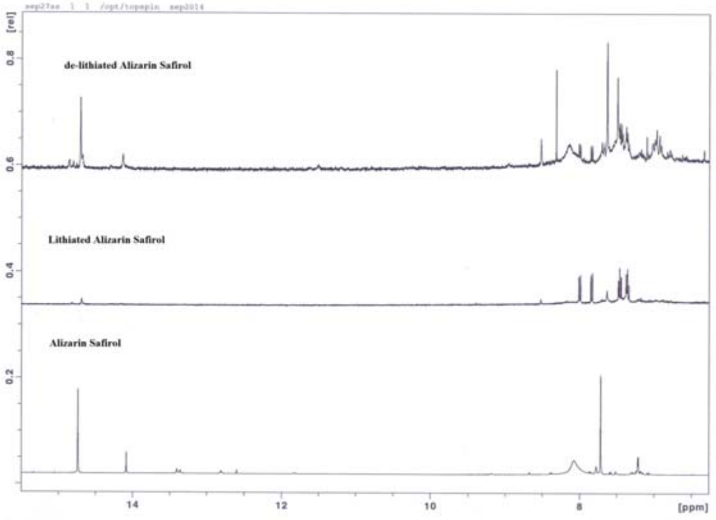


Figure 11: NMR spectra of pristine, lithiated and delithiated AS dye.

c. ***Phthalocyanines and their derivatives.***

We used commercial lithium phthalocynine (LiPC) as electrode material. The cell was fabricated in the following configuration, of anode- Li foil; cathode- LiPC composite (LiPC: Acetylene black= 70:30) on Al foil and the electrolyte- AGM soaked of 1M $LiPF_6$ in EC: DMC (1:1 Volume). The data obtained indicated that pure PC based materials are not very stable and the currents decrease as a function of cycles.

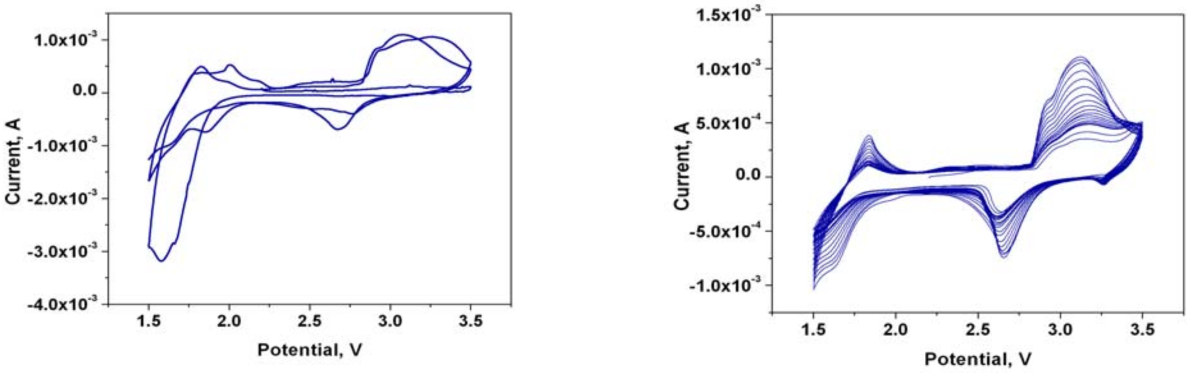


Figure 12: Cyclic voltammograms of LiPC composites in the potential range of 3.5 to 1.5V vs Li/Li^+) at scan rate 2 mV/ sec. The active mass is 3 mg.

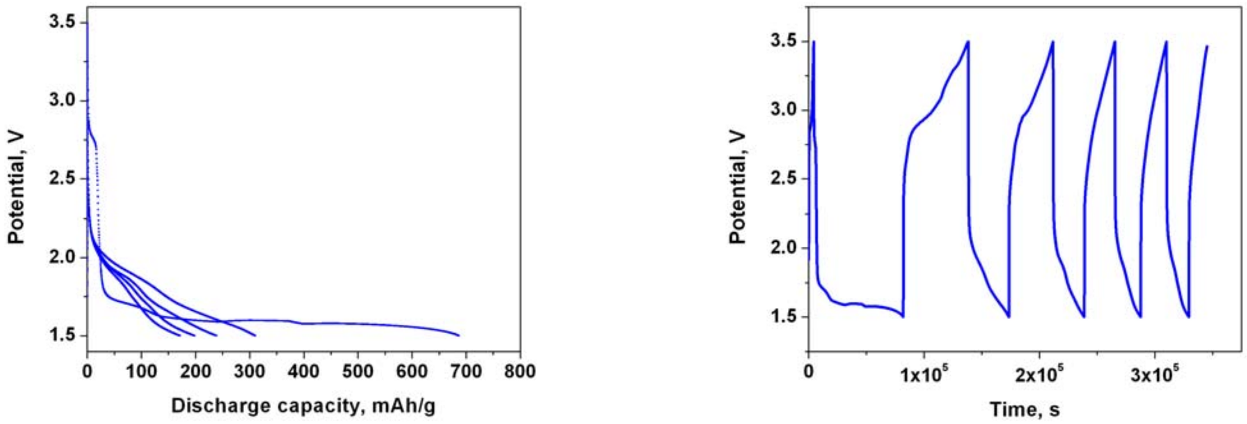


Figure 13: Discharge profiles and capacities of LiPC composites between 3.5 and 1.5 V Li/Li^+.

Summary and way forward

The organic electrode materials studied in the project, ellagic acid, alizarin and phthalocycnines are relatively novel and new in the area of rechargeable lithium battery. Both ellagic acid and AS dye are found to be very promising, with high thermal stability.

- Use of these materials in areas such as Mg and zinc – based batteries are expected to be promising and the studies are underway.
- Density functional theory (DFT) calculations are also being carried out to understand the structure-property relationship.

The following papers are the outcome of the project.

1. *Ellagic acid: A novel organic electrode mateial for high capacity lithium ion batteries*
   G.Subrahmanyam, M. N. K. Harish, and S. Sampath
   Chem. Commun. 2013, *49*,7234

2. *Alizarin Safirol –An organic electrode with high rate capability for rechargeable lithium batteries: Electrochemical and spectroscopic studies.*
   R. Manjunatha and S Sampath
   Communicated, 2015.

3. *Phathalocyanine based reduced grapehne oxide composites for rechargeable lithium batteries*
   Debdyuti Mukherjee and S Sampath
   Communicated, 2015.