Synthesis of activated carbons derived from avocado shells as cathode materials for lithium–sulfur batteries

Wissam Fawaz¹ · Negar Mosavati¹ · Ehab Abdelhamid² · K. Y. Simon Ng¹

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Abstract

Novel mesoporous carbon cathode material for Lithium–Sulfur battery were successfully synthesized from the shells of the avocado fruit. The crystalline structure of the formed carbon was characterized via X-Ray diffraction whilst Scanning Electron Microscopy was used to observe the morphology. The electronic conductivity was determined as a function of pressure and the COOH functional group were quantified via a titration. The mesoporous structure of the formed carbon network allows for good sulfur penetration which is translated by decent electrochemical performance both in terms of cycle life and rate capability. Carbons prepared from waste avocado shells and functionalized with HNO₃ offer a good performance in terms of capacity retention (500 mAh/g of sulfur after 100 cycles). This favorable performance may be attributed to the role of functional COOH groups on the surface of the activated carbon.

Graphical abstract

Keywords Biomass · Lithium–Sulfur batteries · Polysulfides · Carbon · Electronic conductivity

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✉ K. Y. Simon Ng, Sng@wayne.edu | ¹Department of Chemical Engineering and Materials Science, Wayne State University, Detroit, MI 48202, USA. ²Department of Physics, Wayne State University, Detroit, MI 48202, USA.

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1 Introduction

Despite the prevalent use of Lithium Ion Batteries (LIB) in most modern electronics and electric vehicles, the technology itself is rapidly nearing its upper limits in terms of energy density [1]. An energy heaped alternative could be Lithium–Sulfur systems (Li–S) with their theoretical 2500 Wh kg^{−1} energy tab [2–4]. The allure of the Li–S system stems from the low cost of sulfur, its abundance and nontoxic nature, which in turn relaxes many of the restrictions ebbing the current performance of the traditional Lithium Ion Battery cells [5–7].

In spite of its appeal, there are issues that plague Li–S systems:

- (a) Loss of active material during cycling [8]: Upon cycling, some of the polysulfides (Li₂S₈ to Li₂S₄) reduced during the discharge cycle are not recovered to their initial state, but rather remain dissolved in the electrolyte. Some diffuse to the lithium electrode, where they are further reduced via parasitic reactions to even lower order polysulfides such as Li₂S₂ and Li₂S which are insoluble. This continuous loss of active material leads to lower discharge capacity and poor cycle life.
- (b) Once some of the soluble polysulfides diffuse to the lithium electrode and undergo the aforementioned reduction reactions, the parasitic polysulfides, now reduced, would travel back to the sulfur side during a phenomenon known as shuttle. These soluble lithium sulfides would ultimately hinder the lithium ion migration and reduce the conductivity of the electrode [9]. The deposition of layers of the dissolved polysulfides on the negative electrode increases surface impedance and subsequently, these insulating species decrease the columbic efficiency of the cell [10, 11].
- (c) The high resistivity of Sulfur and lithium–sulfides: With a typical resistivity of 2x10¹⁵ Ω.m, sulfur must necessarily be joined to a conductive matrix which would mitigate its lack of conductivity. Carbon is the most widely used material to ameliorate electronic conductivity in most electrochemical systems. These carbons range from simple furnace char [12] all the way to carbon nanofibers [13, 14]. It has been reported that carbons with either a microporous or a mesoporous [15] structure can minimize the polysulfide redox shuttle effect, and many such structures have been studied in Li–S systems [16]. Another strategy is to form composites from sulfur and a conductive polymer [2]. However these tend to be more arduous and lacking in decent capacity [17].

The generally accepted method to alleviate some of the concerns currently associated with Li–S systems is the employment of a carbonaceous matrix to better trap sulfur and assure good conductivity [14].

Conventionally, porous carbons such as superP and graphite have been the carbonaceous support structure of choice for LIB and LI–S systems [18]. Their conductivity could help mitigate the electronically resistive nature of sulfur [19], and their nano-porous structure promotes the physisorption of lithium polysulfides and minimizes the shuttle effect [9]. Recently there is a rising interest in biomass derived carbons due to their tunable surfaces [20] and the ease of enriching those surfaces with various functional groups [21]. While carbons of any source may be activated, the intensive and arduous process of tuning surface pores for each specific application drives the cost of the product and greatly taxes the time requirement [22]. In the case of biomass, the decomposition of cellulose and lignin releases trapped gasses and moisture, which gives rise to porosity without the need for chemical reagents [23] or steam activation. One particular method of interest in the tuning of carbon surfaces for battery applications has been the creation of sulfur trapping pores via reflux in a strong acidic bath [24–26]. Moreover, the acid treatment leads to the formation of hydrated surface oxides on the surface of the carbon, which will enhance the adsorption of inorganic compounds [27].

Biowaste products were extensively investigated for numerous applications such as energy storage [3, 14, 28–31], water filtration [32] and the bulk production of activated carbons [33]. The avocado fruit of the Mexican native (*Persea Americana*) tree is a common waste product of numerous households across the world, which spurred the interest in devising an interesting reuse method for their shells [34].

In this study, avocado shells were first carbonized then treated in nitric acid (HNO₃) to produce mesoporous carbon with a functionalized surface [35]. The effect of the carboxyl surface functional groups on the electrochemical performance of this activated carbon as cathode support material for liquid polysulfide LI–S systems was investigated. Recently, work done at the US Army research laboratory demonstrated an initial capacity of 500 mAh/g by using commercial porous carbon as a host matrix for liquid polysulfides [36]. The cell prepared utilizing nitric acid activated avocado shells carbon has an outstanding initial capacity of 1300 mAh/g with an average decay rate limited to 0.6% per cycle.

2 Experimental

2.1 Materials

Potassium carbonate (K₂CO₃, anhydrous, > 99%) was purchased from Alpha Aesar, Sodium hydroxide

(NaOH, anhydrous, > 98%), nitric acid (HNO₃, ACS Reagent > 90%) urea (CH₄N₂O > 99%), elemental sulfur S₈ (colloidal 99.98%), lithium sulfide Li₂S (99.98%), Bis(trifluoromethane)sulfonimide lithium salt LiN(SO₂CF₃)₂ (> 99%), LiTFSI, triethylene glycol dimethyl ether (TG₃, Reagentplus 99%) and lithium nitrate Li(NO₃) (> 99%) were purchased from Sigma Aldrich and used as received without further alteration.

2.2 Sample preparation

Waste avocado shells were washed with deionized water then dried in air. Using an electric grinder, the dried shells were pulverized into a fine powder. The collected avocado shell powder was heated in a nitrogen rich environment to 800 degrees Celsius at a rate of 10 degrees per minute and held for 2 h. The obtained pristine sample will hereafter be denoted as AvS. An AvS sample was refluxed in nitric acid at 100 °C for 90 min. Post reflux, the sample was washed with copious amounts of DI water to neutralize its pH, and then dried under vacuum for 12 h. In order to study the effect of surface functional groups of the formed carbon on the electrochemical performance, two more samples were prepared with urea and potassium carbonate by mechanical grinding with the AvS carbon at 1:1 weight ratio. The mixtures were subsequently annealed at 800 degrees for 2 h in an inert environment at a heating rate of 10 °C per minutes. These samples were denoted AvS-N, AvS-U and AvS-K respectively and are listed in Table 1. A slurry mixture with an 8:1:1 wt%(Activated carbon, Super P, PVDF) composition was coated on Aluminum foil via a doctor blade. The coated surfaces were dried under vacuum overnight before circular cathode disks with a diameter of 1 cm² and an average carbon loading of 5 mg cm⁻² were cut. Catholyte solution with 0.2 M Li₂S₈, 0.1 M LiTFSI, and 1 M LiNO₃ was prepared by stirring stoichiometric amounts of S₈ and Li₂S into TG₃ at 70 °C for 8 h [10, 37].

A base solution of Lithium Trifluoromethanesulfonate (1 M LiCF₃SO₃) and Lithium Nitrate (0.1 M LiNO₃) was

prepared by stirring stoichiometric quantities of both agents, to obtain a clear homogenous solution to serve as an electrolyte facilitating the ionic transfer between the lithium electrode and the catholyte.

2.3 Characterization

The morphology of the samples was obtained from a field emission scanning electron microscope (SEM, Quanta 400/INCA/HKL). The specific surface area and pore size distribution of the samples were analyzed using a surface area analyzer (ASAP-2010, Micromeritics, America), and they were calculated by the Brunauer–Emmett–Teller (BET) equation. Electronic conductivity of the samples was measured by a two-probe system to determine the dc resistivity. The setup for electronic conductivity measurement is a variation on the design used by Celzard et al. for moderately compressed powder columns [38]. Powder X-ray diffraction (XRD) measurements were conducted on a Rigaku Miniflex diffractometer ($\lambda = 1.54 \text{ \AA}$) with Cu-K α radiation operating at 40 kV and 15 mA. Titration was carried out using an OAKTON pH 11 Series pH/mV/°C Meter. Graphite procured from the TIMCAL Corporation was used without further activation.

2.4 Cells assembly and electrochemical measurements

Electrochemical coin cells were prepared in the following manner: A lithium metal electrode acting as the anode was topped by a separator (celgard 2400 film) soaked in the base electrolyte and pressed against an activated carbon electrode acting as a support for the catholyte. 8 μ L of catholyte solution was added on the positive electrodes.

Coin cells were cycled 100 times at 0.1 C to examine the cycling stability. An additional cell with graphite support was included as a baseline for comparison. The as prepared activated carbon samples were electrochemically tested via galvanostatic discharge–charge tests on a Maccor Model 4200 Automated Test System between the voltage range of 1.5–3 V (vs. Li/Li⁺) at room temperature.

Cyclic voltammogram and electrochemical impedance spectroscopy (EIS) measurements of the cells were obtained using a Gamry potentiostat reference 3000. The voltammetry was performed at a scan rate of 0.1 mV s⁻¹, in the voltage range of 3–1.5 V (vs. Li/Li⁺). EIS measurements were recorded between 1 MHz and 0.1 Hz, and AC amplitude of 10 mV at room temperature.

Table 1 Mesoporous Carbon Prepared from Avocado Shells

Sample	Activating agent	Activation method	Activation time (h)
AvS	None	None	0
AvS-N	Nitric Acid	Reflux	2
AvS-K	Potassium Carbonate	Mechanical grinding	2
AvS-U	Urea	Mechanical grinding	2

Fig. 1 XRD studies of Activated Carbons from Avocado Shells **Table 2** Particle sizes

Sample	D-Spacing (0.22) (Å)	Brag angle	FWHM	Size (Å)
AvS	3.606	24.67	9.81	8.6
AvS-U	3.490	25.50	7.09	12.0
AvS-K	3.550	25.06	4.10	20.7
AvS-N	3.591	24.78	4.75	17.9
Graphite	3.387	26.30	0.49	175.4

3 Results and discussion

The crystal structure of the as prepared carbon was characterized via X-ray diffraction (XRD) (Fig. 1) and shows broadened peaks compared to the diffraction patterns of graphite. The broadening of the peaks at 24.3° and 43.6° associated with the (002) and (100) graphite planes reveals a three-dimensional (001) peak and two (hk) dimensional reflections, as well as a lower degree of graphitization. The lower peak at 24.3° gives a d-spacing of 3.62 Å which is

significantly larger than that of perfect graphite (3.34 Å) [22]. The FWHM for the AvS sample (~9°), when used in the Scherrer equation (Table 2), reveals a crystallite size of 8.6 Å. Given the large disparity from the structure of commercial graphite (175.4 Å), it's been concluded that carbonized avocado shells gave rise to a poorly crystallized, turbostratic structure where layers are parallel but rotated around the c-axis with a low degree of graphitization (−1.9) [39]. The value of the degree of graphitization parameter lies in its relation to the mechanical and thermal properties of the prepared carbon [40], and no impact of its variation was noticed in our electrochemical studies.

The energy dispersive X-ray spectroscopy measurements in (Table 3), suggest that any contaminants present in the pristine carbonized avocado shell have been eliminated and that the carbon to oxygen ratio of the samples is consistent with the affinity to oxygen enjoyed by activated carbons with low degree of crystallinity [41]. The pyrolysis of biomass in an oxygen free environment produces a carbon rich solid remainder that still retains trapped non-condensable constituents such as CO and CO₂ as well as methanol, acetic acid, phenols, hydroxyacetaldehyde,

Table 3 Energy dispersive X-Ray analysis of prepared activated carbons

Sample	Carbon (%)	Oxygen (%)	Sodium (%)	Calcium (%)	Magnesium (%)	Potassium (%)	Si (%)
AvS	70.37	25.67	0.06	3.26	0.40	0.18	0.06
AvS-U	89.41	10.59	0.0	0.0	0.0	0.0	0.0
AvS-K	88.00	12.00	0.0	0.0	0.0	0.0	0.0
AvS-N	75.22	24.78	0.0	0.0	0.0	0.0	0.0
Graphite	98.1	0.6	0.0	1.3	0.0	0.0	0.0

Fig. 2 SEM images of **a** AvS-U, **b**AvS-K, **c** AvS-N, **d** AvS

Table 4 BET surface area & porosity of the prepared carbon samples

Sample	Graphite	AvS	AvS-K	AvS-U	AvS-N
Surface Area (m ² /g)	20.01	1.92	1081.39	131.93	236.63
Micropore Volume (cm ³ g ⁻¹)	0.0005	0.001	0.450	0.065	0.114

anhydrous monosaccharides and other heavy metals [42]. This accounts for oxygen levels in the AvS sample presented in Table 3.

The XRD peaks of the various activated carbons widen in intensity and are slightly shifted downward when compared with graphite. This shift is a result of the 002 interlayer reflection in amorphous carbon as well as the increase in interlayer spacing of the activated samples as revealed in Table 2. The line broadening is not well understood and may be attributed to the creation of defective micro graphene layers lacking in planarity, or with an increase in porosity and specific surface area [22]. The SEM images of the prepared activated carbons shows distorted carbonaceous aggregates rather than ordered graphitic layers (Fig. 2) which agrees with the computed value for the degree of graphitization. Upon activation, there appears to be a fusing of those aggregates into discrete, rigid colloidal entities. No increase in porosity is evident

from the AvS-U sample (Fig. 2a) where structural changes to the carbon are apparent without distinctive features. The SEM image (Fig. 2b) shows that activation of the carbon with K₂CO₃ created micro sized pores which agrees with the porosity shown in Table 4. The solid honeycomb structure apparent in the AvS sample (Fig. 2d) is lost to a relatively solid mass of continuous carbon structure upon nitric acid activation (Fig. 2c).

AvS-N sample (Fig. 2c) shows a reduced porous structure, and flaky layers which vary in size and alignment. Nitric acid activation does not appear to have improved the porosity of the sample as much as alter the structural arrangement of the carbonaceous layers as reported elsewhere [43].

Topology, surface area and surface functional groups of activated carbons are major influences on resistivity [38, 44–46]: Carboxylic functional groups latch to the diamond like Sp³ carbons which are sparingly available in biomass carbons. This does not affect the electronic conductivity of the activated carbons since that normally only involves Sp² electrons [25, 38, 45]. Porosity plays an inverse role with conductivity since free moving electrons following the conductive path of their flow, are forced to overcome an increasing number of particle voids and discontinuities in their conductive path [31, 38, 44–49]. This effect is visible in the prepared activated carbon samples as the

Fig. 3 DC resistivity of prepared activated carbons

conductivity (Fig. 3) increases with pressure, since carbon aggregates get rearranged into a state that increases contact between particles.

Because of the ordered structure of commercial graphite and the lack of functional groups on its surface, little change is observed in its electronic conductivity as the pressure shifts from low to high. For activated carbons however, dc resistivity drops at higher pressure as the conductive crystalline agglomerates become packed close enough to allow hopping of electrons [48].

The presence of carboxylic groups on the surface of the nitric acid functionalized carbon [50] was quantized via a modified Boehm method of titration of a 0.01 M sodium hydroxide solution until the titrant (AvS-N + DI water) reached a neutral pH. The presence of 0.47% of COOH per mol of activated carbon was calculated. The creation of these oxygenated groups on the surface of the prepared carbon appear to be presented at the expense of the availability of Sp^2 carbon on the surface, which in turn hindered the electronic conductivity of the AvS-N sample (Fig. 3). It has been reported that activation of carbons via other reactant, creates hydroxyl and alkenes groups (K_2CO_3) [51] or pyridine surface groups (Urea) [52].

Cycling performance of the Li-S cells was assessed by 100 discharge cycles shown in Fig. 4. AvS-N sample shows an initial decay from 2100 to 1300 mAh/g. Capacity continues to fade at an average rate of 4% per cycle up until the 20th cycle where the rate reduces to an average of 1% or less per cycle. Graphite suffers an initial capacity fade of 9% and stabilization to 1.5% decay rate per cycle occurs around the 32nd cycle. The other activated carbon samples stabilize after the 25th cycle and follow similar

Fig. 4 Specific capacity of activated carbons at 0.1 C rate

capacity drop of around 0.5% all the way through the 100th cycle.

The AvS-N sample was able to retain 47% of its initial capacity of 1300 mAh g^{-1} after 100 cycles to terminate at a capacity of 529.9 mAh/g.

In order to qualitatively investigate the ability of the activated carbon cathode materials to adsorb and trap polysulfide species, each type of carbon was mixed with a 0.02 M dissolved Li_2S_8 solution and stirred for (8 h). the carbon particles were separated from the dissolved Li_2S_8 particles using a centrifuging technique. The solution containing the AvS-N mixture showed the most adsorption of polysulfide species, qualitatively assessed by the change of solution color. The increased adsorption can be attributed to induced surface charge of the carboxyl groups on the surface of the AvS-N sample, which enhances the binding of sulfur to the C-C bond [53]. The solutions containing the other carbon samples showed significantly less discoloration. A photo of the prepared solutions, along with appropriate stoichiometry can be found in the supporting material section.

The transformation of polysulfides into high orders hinges on the ability of the conductive matrix to deliver decent adsorption [54] which in turn leads to an amelioration in the width of the voltage discharge plateau. Galvanostatic charge-discharge profiles of the prepared carbon electrodes and the commercial graphite one at 0.1 C rate and a voltage window between 1.5 and 3.0 V are shown in Fig. 5. The AvS-N sample shows the widest plateau amongst all samples considered. This is further indication that AvS-N possesses high adsorption capacity for the catholyte. The apparent plateaus corresponding to the conversion of Li_2S_8 to higher and lower order polysulfides respectively species [55, 56] are

Fig. 5 Galvanostatic charge discharge profile: **a** 5th cycle, **b** 100th cycle

Table 5 Capacity retention and rate of decay

Sample	Rate of decay at cycle (per cycle) (%)	Capacity after 100 cycles [mAh/g]
AvS	1.36	135.4
AvS-K	1.71	102.5
AvS-U	1.42	133.6
AvS-N	0.92	529.9
Graphite	0.72	247.6

more pronounced in the AvS-N sample when compared to the other carbons. Discharge profiles for the 100th cycle are presented in Fig. 5b to demonstrate that the

lower plateau (at 2.1 V) is noticeably more extended for AvS-N than the other samples due to AVS-N's better ability to continue the polysulfide conversion. Noticeably, the other activated carbons fail to form a discernible plateau at the 100th cycle as the polysulfide conversion reaction diminished. Avocado shells activated with nitric acid are clearly more apt for the polysulfide conversion and it is reflected in their excellent capacity (Table 5).

Impedance spectroscopy measurements of fresh cells made from prepared carbon materials, having identical sulfur, carbon and catholyte loading, were computed (Fig. 6). Similar measurements were conducted on those cells post cycling and the results are presented in the supplementary material. Table 6 shows the values for the charge transfer resistance (R_{ct}) which is the radius

Fig. 6 Initial Electrochemical Impedance Spectroscopy of all carbonaceous samples employed

of the semi-circle on the Nyquist plot's high frequency region [57]. After the addition of 10% conductive superP carbon to the slurry to increase electronic conductivity, it was found that differences in the R_{ct} value exist between activated carbon samples which may be attributed to their carbonaceous structure and surface functional groups. Among all activated carbons, the AvS-N sample exhibit the least change in R_{ct} values post cycling. This is an indication of better ionic diffusion into the carbonaceous structure than the other samples [58]. The shift towards higher values of R_{ct} after cycling is due to the creation of insoluble species such as Li_2S_2 and LiS which ebb the cyclability of the cell [59]. AvS and AvS-U samples exhibit large charge transfer resistances that hinder their suitability for LiS applications.

Despite AvS-N having a relatively high charge transfer resistance, its better cycle life is likely due to its superior ability to adsorb dissolved polysulfide species in the system. (see supplementary material).

To gain a better understanding of the oxidation and reduction reactions taking place inside these cells, CV curves of the cells prepared with identical loading of sulfur and activated carbons show the first, second and third voltammograms at 0.1 mV s^{-1} in the range of potential

between 1.5 and 3.0 V. Two reduction peaks and one oxidation peak are presented at 2.37 V, 1.9 V and 2.5 V respectively (Fig. 7). The reduction of the liquid Li_2S_8 into intermediary subspecies Li_2S_x ($4 < x < 6$) occur during the high voltage cathodic peak while the further reduction into insoluble Li_2S_2 and Li_2S happens during the lower voltage cathodic peaks [60]. It is noticeable that the anodic peaks corresponding to the graphite sample lose intensity as the cell cycles going from 43 to 24 mA which is an indication that the amount of active material capable of being oxidized is diminishing with cycling. The AvS-N sample exhibits a stable behavior across all three CV cycles, with little discernible change in the current response due to its good electrochemical stability, and its ability to adsorb dissolved polysulfide species.

4 Conclusions

The effect of surface functionalization on the capacity of the lithium sulfur system was demonstrated through the synthesis of new cathode host material from avocado shells carbon. Cycle life extension and stabilization was achieved through introduction of carboxyl surface groups via nitric acid reflux.

AvS-N carbon material shows good capacity retention and a capacity of 529.85 after 100 cycles which is 72.6% higher than commercial graphite.

The structure and ameliorated surface of nitric acid functionalized activated carbons are apt conductive host matrix for the improvement of the sulfur utilization and at thwarting the dissolution of polysulfides into the electrolyte.

Table 6 Electrochemical Impedance data: The charge transfer resistance

Sample	R_{ct} -Init [Ohm]	% increase post cycling (%)
AvS	88.3	167.5
AvS-K	56.8	45.23
AvS-U	74.3	54.5
AvS-N	53.4	38.67

Fig. 7 Cyclic Voltammogram of Li-S cell made with: **a** graphite anode, **b** AvS-N anode

Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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