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Humic Acid-Derived Mesoporous Carbon as Cathode Component for Lithium-Sulfur Battery

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Ordered mesoporous carbon has successfully been synthesized using SBA-15 silica as the hard template and, for the first time, humic acids as the carbon source. The obtained carbonaceous material features hexagonally ordered pores with an average diameter of 7.6 nm and a high specific surface area of 670 m^2g^{-1}. The synthesized carbon has been applied as the sulfur cathode component in Li-S cells. At 20% content in the composite cathode and no auxiliary conducting additives, the material resulted in significantly advantageous specific capacities over conventional carbon black and commercial mesoporous carbon CMK-3 (up to 1200 $mAhg^{-1}$) as well as improved cycling stability and rate capability. The effect has been attributed to a favorable morphology and porous structure of the humic acids-derived carbon.

Keywords: mesoporous carbon; humic acids; lithium-sulfur battery; hard template synthesis; mesoporous silica SBA-15

1. INTRODUCTION

Energy utilization increases rapidly together with the population growth as well as with technological and social developments. Inevitably, there is an ever growing need for more efficient ways of storage, conversion and management of the energy that we have for our disposal [1 - 3]. As far as electrochemical electricity storage systems are concerned, current state-of-the-art Li-ion chemistries based on the application of insertion-type electrodes have almost reached the upper limit in terms of energy density. Among various types of prospective rechargeable systems, lithium-sulfur batteries are widely regarded as one of the most promising [4, 5]. Unlike conventional Li-ion systems, Li-S batteries utilize metallic lithium which is characterized by a very high electronegativity and the lowest density among all metals, leading to the highest theoretical specific capacity of 3861 mAh g^{-1}. Sulfur, one of the most abundant elements in the earth crust, exhibits a theoretical capacity of 1673 mAh g^{-1}, which is an order of magnitude higher than those of the transition-metal oxide cathodes. Thus, Li-S batteries can potentially reach unparalleled gravimetric and volumetric energy densities of 2500 Wh kg^{-1} and 2800 Wh L^{-1}. Moreover, sulfur is considered to be safer for the user and environment as compared to battery chemistries utilizing highly toxic and expensive heavy metals [6, 7].

Nevertheless, there are still several issues impeding practical application of rechargeable Li-S batteries [8]. High resistance of sulfur and lithium polysulfides formed during cycling is one of the most important. The other problematic issues include short cycle life, low charging efficiency and a high self-discharge rate. These issues are related to the dissolution of lithium polysulfides in liquid electrolyte and redox shuttle mechanism between sulfur cathode and Li anode [9, 10]. Much efforts have been dedicated to improve the electrochemical performance of sulfur cathodes [11, 12, 13]. Various type of carbon materials, such as mesoporous carbons [14], microporous carbons [15], porous carbon fiber [16], hollow carbon spheres [17] and self-assembled structures [18] have been applied to both enhance the electronic conductivity of the sulfur composite and hinder the dissolution of polysulfides into the electrolyte. Nevertheless, there is still urgent need to look for novel carbonaceous materials with precisely tailored morphology.

It is known that biomass is a rich resource of carbon precursors and usually the synthetic routes are simple, inexpensive and scalable. Humic acids are an example of organic substance playing important role in the ecosystem, abundant in nature and easily recoverable from soil by means of simple extraction with alkali media [19]. Very recently, humic acids have been applied in electrochemical capacitors as an agent providing additional pseudocapacitance [20]. In the present work, ordered mesoporous carbon prepared from humic acids is for the first time reported as functional component of sulfur cathodes for Li-S batteries. The paper aims at describing how unique morphology of this material enables reversible accommodation of large amounts of sulfur species upon charge/discharge of a Li-S cell.

2. EXPERIMENTAL

Mesoporous silica SBA-15 was synthesized according to literature procedure [21] using triblock copolymer Pluronic P123 (SigmaAldrich) as structure directing agent and tetraethylorthosilicate TEOS (AlfaAesar) as the silica source. After calcination, the obtained material was used as the hard template for the synthesis of ordered mesoporous carbon according to the following procedure. 1 g of purified humic acids (Rosier S.A., Belgium) and 1 g of SBA-15 were mixed together in 50 ml of demineralized water. After 12 h water was evaporated and mixing was repeated with fresh portion of water. After next 12 h water was again evaporated and the sample was dried under vacuum at 110°C for 24 h. The pyrolysis was carried out in a quartz tube furnace in argon atmosphere at 800°C for 1 h. The carbon-silica composite obtained in this process was subsequently washed twice with 5 wt.% HF solution to remove the silica template. The resulting template-free carbonaceous product, designated as HAMC, was subjected to drying in vacuum at 110°C for 24 h. Conventional ordered mesoporous carbon CMK-3 has been synthesized according to procedure described in literature [22].

Scanning and transmission electron microscopy images were taken with Zeiss EVO 40 and JOEL JEM 1200 EX, respectively. Low-angle X-ray diffraction patterns were recorded with PANalytical X'Pert^3 Powder. Nitrogen adsorption isotherms were obtained with the application of ASAP2010 porous structure analyzer (Micromeritics). Thermogravimetric analysis was conducted using Netzsch STA409 CD instrument. Carbon content was determined using Vario Micro C/H/N/S analyzer.

The positive electrodes for the electrochemical tests were prepared by casting the slurry containing the active material onto current collectors (aluminum or stainless steel foil). The slurry consisting of sulfur (SigmaAldrich), mesoporous carbon from humic acids and binder (sodium carboxymethyl cellulose - SigmaAldrich) was prepared by dry-homogenization of the components (at a wt.% ratio 70:20:10) followed by dispersing in demineralized water. The resulting cathodes were dried at 60°C under vacuum for 24 h. The cathodes were assembled in an argon-filled glovebox (MBraun LABstar) in Swagelok-type cells with metallic lithium as the anode and Celgard 2400 as the separator. The electrolyte was a solution of lithium trifluoromethanesulfonate (0.5 M, SigmaAldrich) and of $LiNO_3$ (0.5 M, Fluka) in a 1:1 mixture of 1,2-dimethoxyethane (DME, SigmaAldrich) and 1,3-dioxolane (DOL, SigmaAldrich). The cells were galvanostatically charged/discharged at a current density of 0.02, 0.06 and 0.1 C between 1.7 and 2.7 V vs. Li/Li^+. Cyclic voltammetry experiments were carried out at the scan rate of 0.05 mV s^{-1} also between 1.7 and 2.7 V. All electrochemical measurements were carried out using multi-channel VMP3 potentiostat/galvanostat (Bio-Logic).

3. RESULTS AND DISCUSSION

Ordered mesoporous carbon (HAMC) has been synthesized using SBA-15 silica as hard template and humic acids as the carbon source. Obtained carbon is an inverse replica of SBA-15 silica. The low-angle XRD patterns of the SBA-15 silica and HAMC carbon are shown in Fig. 1.

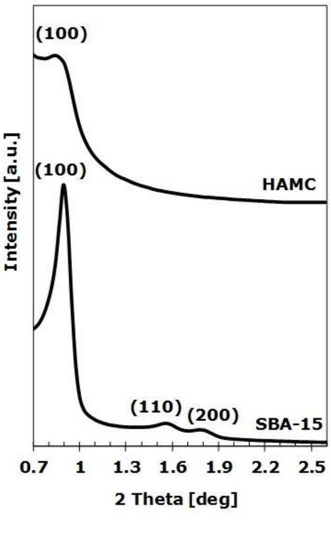

Figure 1. Low-angle XRD patterns of HAMC carbon and SBA-15 silica.

The mesoporous silica exhibits three well-resolved peaks, which can be ascribed to the (100), (110) and (200) reflections from a two-dimensional hexagonal p6mm pore system symmetry. The d value (which is the d_{100} lattice spacing in the two-dimensional hexagonal pore arrangement and can be calculated from the respective scattering angle θ by Bragg´s law) corresponding to the (100) reflection is 7.4 nm. The HAMC carbon is expected to be the negative replica of SBA-15. In contrast to the low-angle diffraction signature of the SBA-15 silica matrix, HAMC carbon exhibits only (100) reflection. The relative intensity of the (100) reflection is decreased in comparison to SBA-15 silica due to negative interferences, which is typical of this structure. The d value for HAMC carbon is 7.8 nm, comparable to the SBA-15 silica matrix within experimental error. The obtained pattern indicates for a short-range order of mesopores in the carbon as opposed to a full hexagonal order of the silica template.

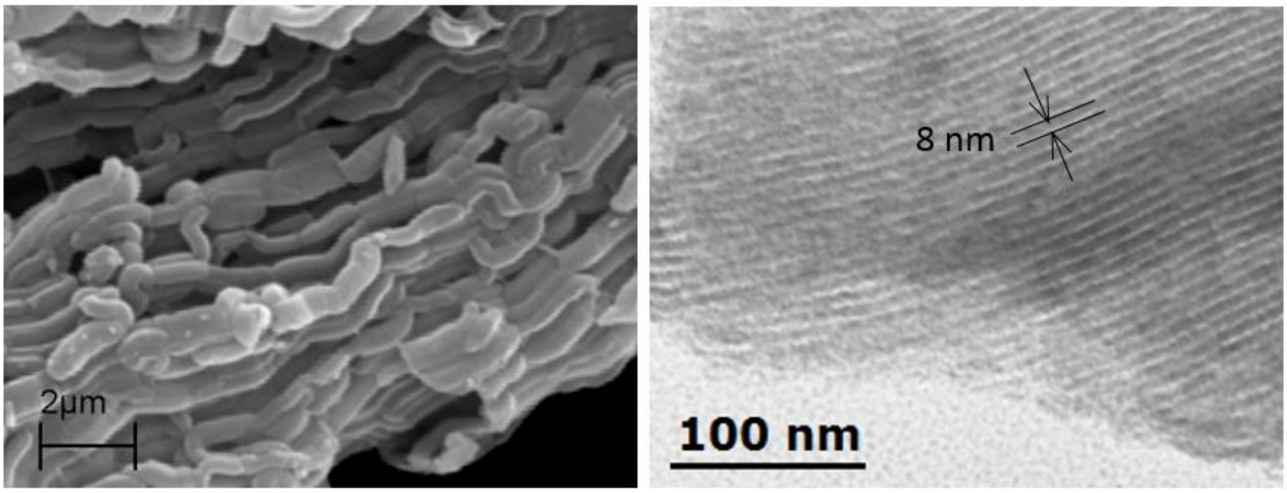

Figure 2. SEM (left) and TEM (right) images of ordered mesoporous carbon HAMC.

The SEM and TEM images of obtained mesoporous carbon (Fig. 2) show that HC particles have the same morphology as that of the SBA-15 silica particles. The structure of SBA-15 consists of the hexagonal arrangement of cylindrical mesoporous tubes 7 nm in diameter. The transmission electron micrograph images of the obtained carbon show the 8 nm in diameter cylindrical pores with parallel arrangement.

Fig. 3. shows thermogravimetric analysis (TGA) curve for the obtained mesoporous carbon. The sample exhibits former 3 wt% loss due to removal of water and latter 94 wt% loss as the carbon is burned off. Carbon content was also confirmed by elemental analysis (see Table 1).

The nitrogen sorption isotherm of HAMC is shown in Fig. 4 (in the inset - pore size distribution curve). As can be seen, HAMC reveals IV-type isotherm with a H1-type hysteresis loop, characteristic for mesoporous materials with cylindrical pores. The specific BET surface area of HAMC was found to be 670 m^2 g^{-1}, which is comparable to SBA-15 (740 m^2 g^{-1}).

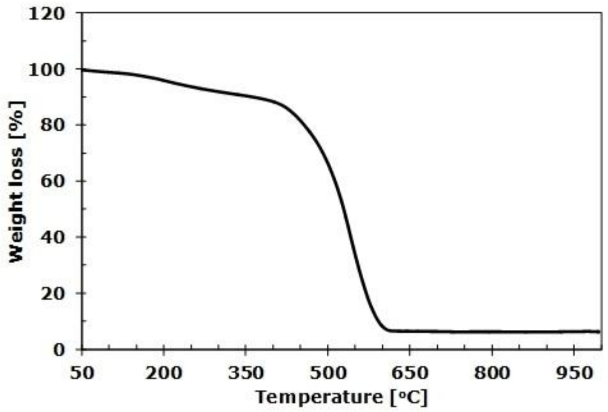

Figure 3. Thermogravimetric analysis of HAMC carbon.

Table 1. Elemental analysis of humic acid and HC carbon (wt.%).

Sample	C	H	N	S	Ash
Humic acid	44.6	3.4	1.2	0.3	-
HAMC carbon	90.2	1.5	2.7	0.6	6

The total pore volume is 1.5 cm^3 g^{-1} and the BJH average pore diameter calculated from desorption branch is 7.6 nm. Both XRD, TEM and N_2 adsorption techniques together provide evidence that an ordered mesoporous carbon has been synthesized.

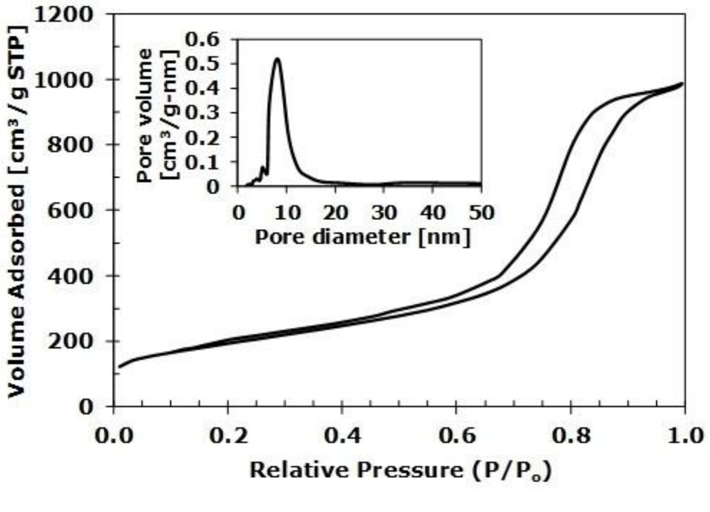

Figure 4. Nitrogen sorption isotherm and pore size distribution (inset) of ordered mesoporous carbon HAMC.

The described humic acids-derived ordered mesoporous carbon HAMC has been applied as sulfur cathode component in Li-S cells. Importantly, no additional conducting agent was added, which is a common practice in other works on carbons for Li-S batteries [23-25]. Thus HAMC plays double role of the conducting agent and reservoir of sulfur and polysulfides. Fig. 5a shows the first three CV cycles of a Li-S cell with sulfur/HAMC cathode. Two cathodic (reduction) peaks are observed at ca. 2.3 V and ca. 2.0 V upon both the first and subsequent cycles. The first peak can be assigned to the reduction of sulfur to Li polysulfides (Li_2S_n, $2 < n < 8$) and the second peak may be assigned to the reduction of Li polysulfides to insoluble Li sulfides such as Li_2S_2, Li_2S. Upon anodic sweep an oxidation peak at ca. 2.4 V is observed, corresponding to the reverse conversion of Li_2S_2 and Li_2S to polysulfides and sulfur. 2nd and 3rd cycle curves overlap almost exactly, suggesting high reversibility degree.

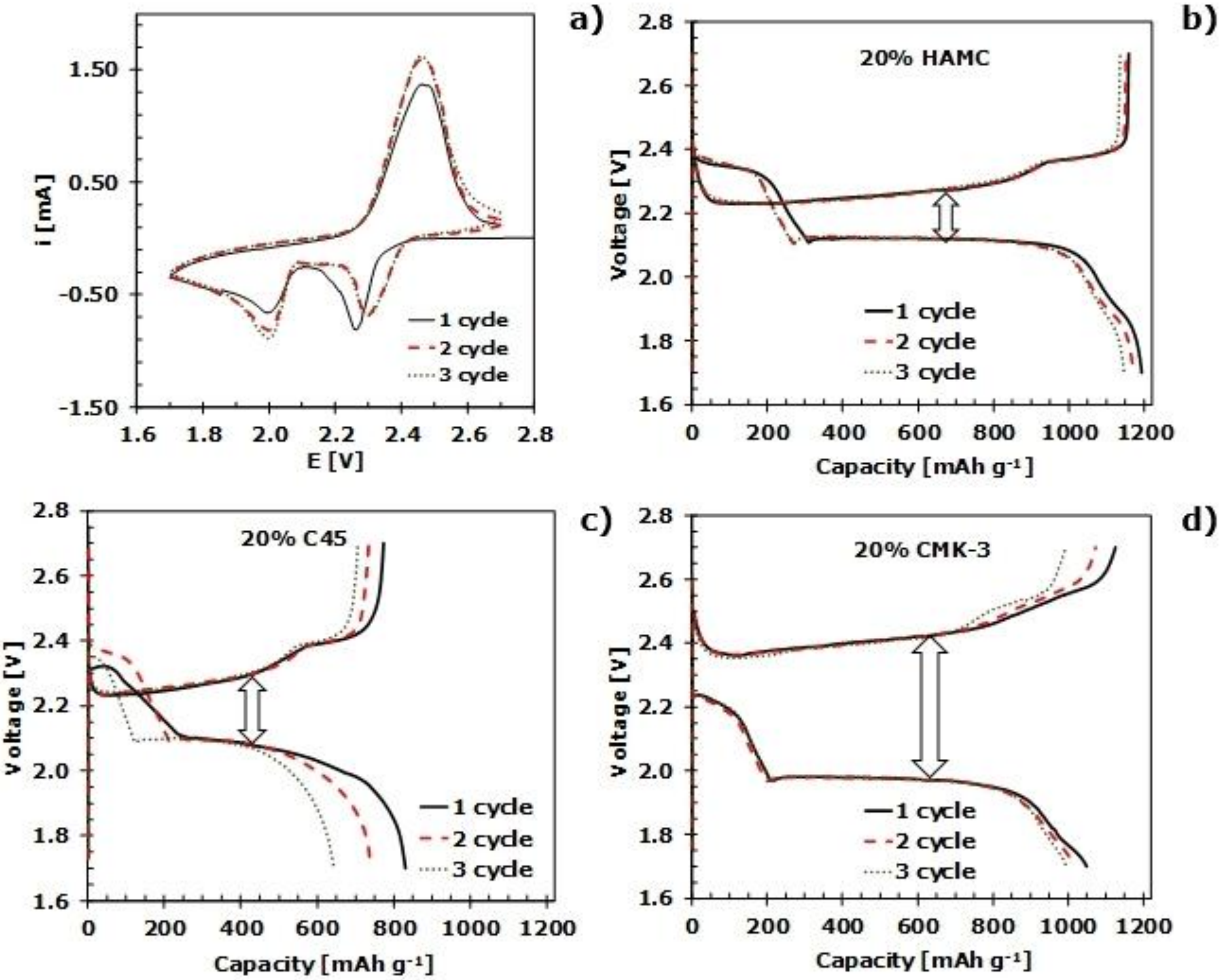

Figure 5. a) Cyclic voltammograms of a Li-S cell with sulfur/HAMC cathode; b-d) Galvanostatic charge/discharge profiles of a Li-S cells with HAMC, C45 and CMK-3 carbons, respectively.

Galvanostatic charge/discharge curves in the first 3 cycles for HAMC are shown in Fig. 5b. As benchmarks, analogously recorded characteristics of commercial C45 carbon black and a CMK-3 mesoporous carbon are presented in Figs 5c and 5d, respectively. Upon the first discharge the composite sulfur cathode with HAMC delivers a very high capacity of 1200 mAh g^{-1} at 30 mA per gram of sulfur (corresponding to 0.02 C rate). The coulombic efficiency in the first discharge/charge cycle is 97%. In the second and third cycles, still large reversible capacities of ca. 1170 mAh g^{-1} are observed with 98% coulombic efficiency. For comparison, composite sulfur cathode with C45 carbon black delivered 830 mAh g^{-1} in the first discharge and the capacity was found to significantly decrease upon subsequent charge/discharge cycles (see Fig. 5b). Interestingly, CMK-3 also exhibited a markedly lower first cycle capacity of 1040 mAh g^{-1} in the first cycle with 93% coulombic efficiency (see Fig. 5d).

In Figs 5b-d the sizes of hysteresis between the charge and discharge curves have been shown with arrows. Evidently, HAMC gives rise to the lowest hysteresis as compared to benchmarks, suggesting the best kinetic conditions of ionic transport. This observation can explain, to a large extent, the favorable performance of HAMC in terms of capacity and cyclic stability.

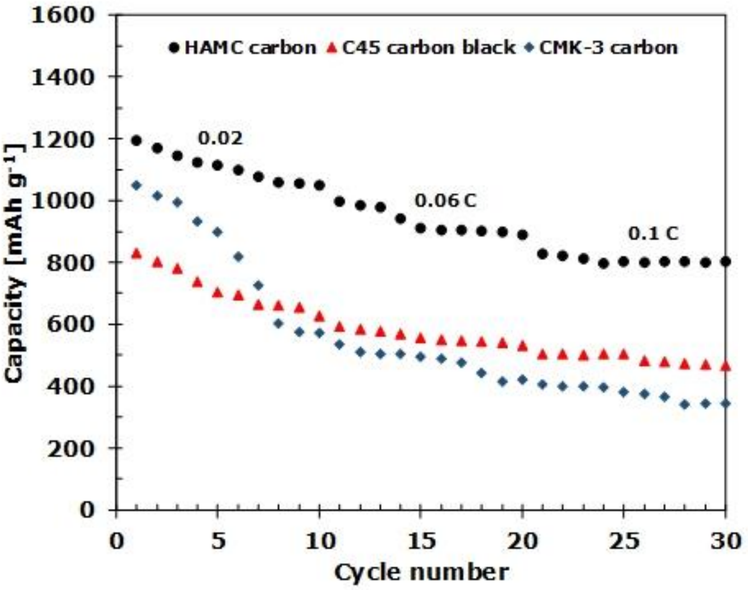

Figure 6. Rate performance of Li-S battery with different sulfur cathode composition.

Fig. 6 compares high rate behavior of composite sulfur cathodes with the three carbons. It can be seen that HAMC gives rise not only to the highest initial capacity at low rate but also the best performance at higher rates and the best capacity stability. At 100 mA g^{-1} HAMC still exhibits over 800 mAh g^{-1} which is nearly twice as much as in the case of C45 and CMK-3, both showing besides a visible capacity loss.

The evidence shows that the described carbon provides a very favorable support for sulfur and sulfur species as well as an effective conducting agent in composite sulfur cathodes for Li-S batteries. Generally, mesoporous carbons tend to perform better as compared to simple carbon powder. Early work of Ji *et al.* [14] reported the performance of a CMK-3/S composite, presenting similar sulfur specific capacities to those observed in the present work (ca. 1000-1300 mAh g^{-1}). However the authors applied additional carbon as conducting agent, which limits the practical energy density of this approach and makes their results incomparable to this work. More recently, Jin et al. [26] coated CMK-3/S composite with polyaniline and observed ca. 1000 mAh g^{-1} in initial cycles, however with fast capacity loss upon subsequent cycles, also with the usage of additional conducting agent. Reports on the application of proprietary mesoporous carbons are very scarce, if not non-existent.

The differences in electrochemical performance between HAMC and CMK-3 can be provisionally ascribed to different degree of structure perfection, specific surface areas as well as total pore volume and pore size distribution. Apparently, short range order with a significant amount of structural imperfections may favor faster mass transfer kinetics. Also relatively large pore diameter observed for HAMC (7.6 nm, in contrast with 3.8 nm for CMK-3) can facilitate sulfur species accommodation and release.

4. CONCLUSIONS

Preliminary results show that, in analogous experimental conditions, mesoporous carbon with short range order obtained by hard template synthesis from humic acids performs better than typical carbon black and, particularly importantly, also than conventional mesoporous carbon, in terms of capacities at of low to medium current loads and cyclic stability. There is certainly room for further optimization of the system’s high rate capability by tailoring the electrode manufacturing procedure. The study may suggest that humic acids as carbon precursor gives rise to a favorable morphology and porous structure suitable for accommodating intermediate lithium sulfides that form upon the cathode charge and discharge.

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