Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Free Standing Acetylene Black Mesh to Capture Dissolved Polysulfide in Lithium Sulfur Batteries

Tae-Gyung Jeong[a], *Young Hoon Moon*[a], *Ho-Hwan Chun*[b], *Hyung Sun Kim*[c], *Byung Won Cho*[c] *and Yong-Tae Kim*[a]*

[a]School of Mechanical Engineering, Pusan National University, Busan 609-735, Korea
E-mail: yongtae@pusan.ac.kr

[b]Global Core Research Center for Ships and Offshore Plants (GCRC-SOP), Pusan National University, Busan 609-735, Korea

[c]Center for Energy Conversion, Korea Institute of Science and Technology, Seoul 130-650, Korea

***Preparation of carbon meshes*:**

One gram of acetylene black (Denka black, Denki Kagaku Kogyo) or meso carbon micro beads (MCMB, Osaka Gas) was dispersed in ethanol (5 ml) by sonication for 10min. And then it was mixed with 1.66g of polytetrafluoroethylene (PTFE, 60 wt% dispersion in H_2O, Aldrich) using a homogenizer to 5000rpm for 20min. To form the carbon mesh, the mixture of carbon and PTFE was aggregated using a mortar and pestle. The carbon mesh was dried to remove ethanol and moisture in a vacuum oven (80℃) for 12h. For thickness control, the carbon mesh was pressed until about 200um by rolling.

***Characterization*:**

SEM and EPMA image were taken using a HITACHI s-4100 (accelerating voltage 5kV) and a JXA-8500F (accelerating voltage 10kV), respectively. Elemental mapping analysis was performed using energy-dispersive X-ray spectroscopy in the EPMA.

***Electrochemical measurements*:**

To prepare the cathode for lithium sulfur battery, active material (sulfur, 0.18g) was mixed with conductor (Super P, 0.06g) and binder (poly vinyliden fluoride, 0.06g) using a ball-mixer (pulverisette 23) in N-methyl-2-pyrrolidinone to form a slurry. The slurry was coated on aluminum foil using doctor blade and dried in a vacuum oven at 60^{O}C for 12h. The thickness and the diameter for sulfur cathode was 18 μm and 15 mm, respectively. Also, the sulfur content in cathode was 60 wt% and the loading amount was 1.12 mg/cm^2. 2032-type coin cells were assembled in a drying room using lithium foil on copper as the counter electrode. Polyethylene membrane used as the separator was obtained from SK-inovation Inc. Carbon mesh was inserted between working electrode and separator. The electrolyte used was 1M lithium bis(trifluoromethane sulfonyl)imide in tetra(ethylene glycol)dimethyl ether and 1,3-dioxolane (1:1 v/v) containing 0.2M $LiNO_3$. The electrolyte volume of 120 μl was injected into the 2032 cell. Galvanostatic cycling was carried out using a battery tester (Maccor 4300K) from 1.5-2.8V versus Li^+/Li at 0.1C (1C=1675 mA g^{-1}). Cyclic voltammetry (CV) measurements were performed on solatron 1286 at a scan rate of 0.1mV s^{-1}.

***Electrolyte uptake experiments*:**

We have measured the weight change before and after soaking the electrolyte into the carbon mesh with enough time and calculated the uptake amount with the following formula[1]:

Uptake (%) = $(W_2-W_1)/W_2 \times 100\%$

where W_1 and W_2 is the weight of carbon mesh before and after soaking the electrolyte, respectively. This method cannot reflect the exact porosity, but it is good enough for a relative comparison of porosity between two samples. While the uptake amount for the MCMB mesh was just 3.73%, that for the acetylene black mesh was 53.73%, about 14 times higher uptake amount than the MCMB mesh. Hence, it is readily expected that the acetylene black mesh can provide a higher surface area and therefore higher possibility to capture the dissolved polysulfide from the sulfur cathode.

***Controlled experiments with a sulfur/carbon composite cathode having extremely high content of carbon* :**

It is widely recognized that the increase of carbon content in the sulfur/carbon composite cathode can lead to the enhancement of lithium sulfur battery performance, because the increased conductivity of cathode can give rise to the increased utilization of insulating sulfur[2-4]. Indeed, since our approach, the insertion of acetylene black mesh, can be considered to be another modified method of carbon content increase in the cathode, the performance enhancement might be attributed to a simple effect of carbon content increase rather than a unique effect of acetylene black mesh insertion. Hence, in order to finally confirm the unique effect of the acetylene black mesh, we have prepared a sulfur/carbon composite cathode having extremely high content of carbon (60 or 80% of carbon, while just 10% of sulfur active materials) and carried out a battery performance test in the same condition. As can be seen in Figure S5, the capacity and the cycle performance were very poor and could not be compared to the results obtained from the LSB-AM at all. In particular, the lower plateau at around 2.0 V corresponding to the formation of lithium sulfide from polysulfide was almost vanished, indicating that most polysulfides were dissolved out into electrolyte and could not be recovered into lithium sulfide at the carbon lattice in the cathode[5]. That is, the carbon-rich cathode was not efficient at all to capture the dissolved polysulfide, even though enough surface area of carbon was provided in the inside of cathode. It is likely that there must be a concentration gradient of dissolved polysulfide in the interface between cathode and electrolyte, and therefore the diffusion of polysulfide into electrolyte is inevitable to some extent. In such situation, to capture the dissolved polysulfide is much more advantageous at the electrolyte in the vicinity of cathode surface than at the cathode itself. Hence, we can evidently conclude that a simple increase of carbon content in the cathode cannot lead to an effective polysulfide capture and therefore the performance enhancement is solely due to the effect of acetylene black mesh insertion.

References:

1. Z. Y. Cui, Y. Y. Xu, L. P. Zhu, J. Y. Wang and B. K. Zhu, *Ionics*, 2009, **15**, 469-476.
2. J. Shim, K. A. Striebel and E. J. Cairns, *J Electrochem Soc*, 2002, **149**, A1321-A1325.
3. C. W. Park, H. S. Ryu, K. W. Kim, B. Y. Hur, K. K. Ch, J. H. Ahn, J. Y. Lee and H. J. Ahn, *Met Mater-Int*, 2004, **10**, 375-379.
4. C. D. Liang, N. J. Dudney and J. Y. Howe, *Chem Mater*, 2009, **21**, 4724-4730.
5. S. E. Cheon, S. S. Choi, J. S. Han, Y. S. Choi, B. H. Jung and H. S. Lim, *J Electrochem Soc*, 2004, **151**, A2067-A2073.

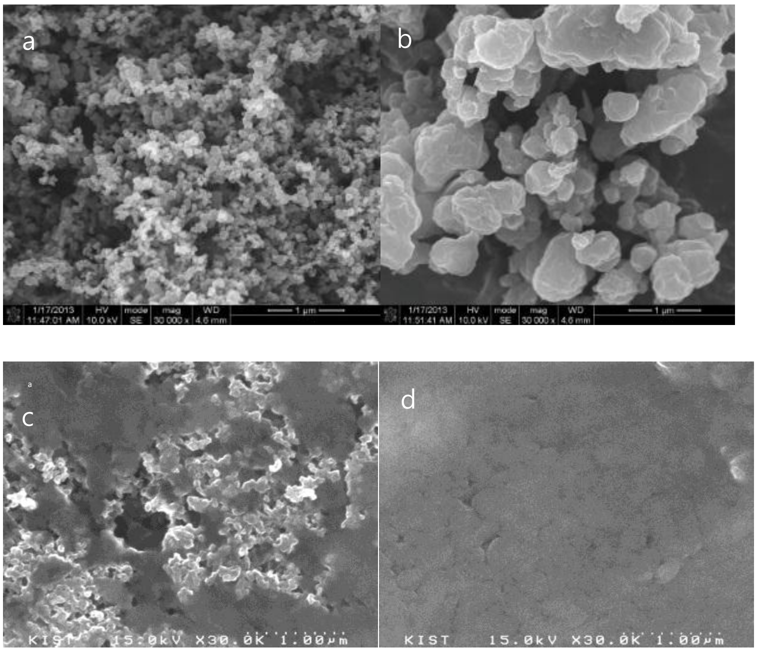

Figure S1. Morphology of Carbon and Carbon mesh. SEM image of (a) original acetylene black and (b) MCMB, (c) acetylene black mesh, (d) MCMB mesh.

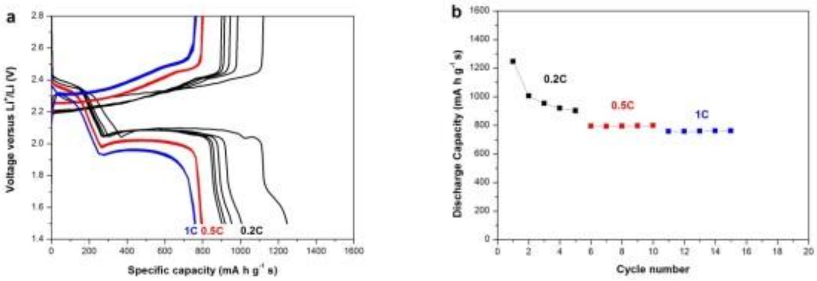

Figure S2. Rate capability of LSB-AM. (a) Voltage profile and (b) cycle performance of LSB-AM at various C-rates from 0.2 to 1C.

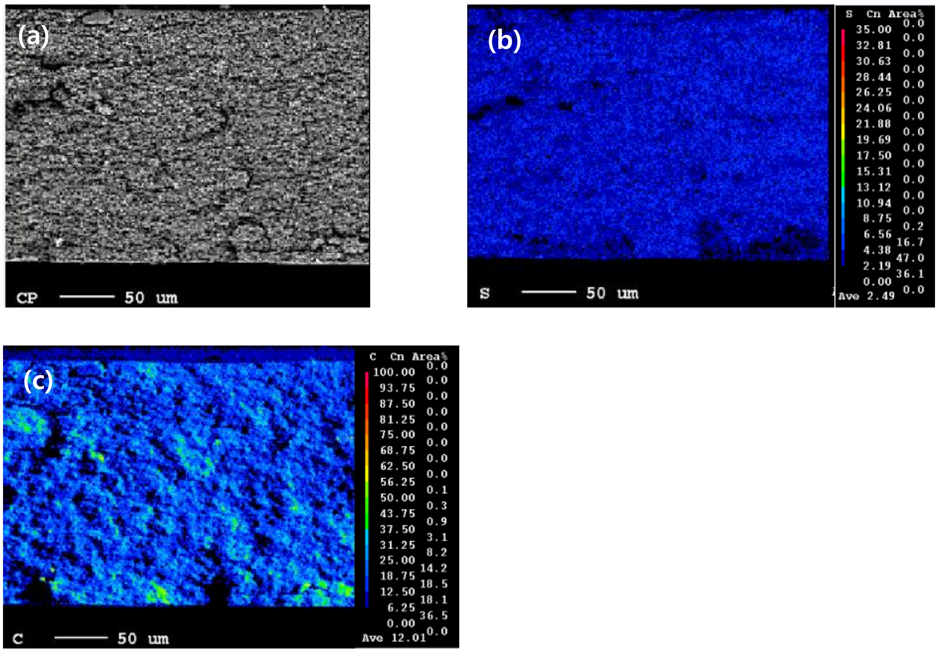

Figure S3. Electron probe micro-analyzer of acetylene black mesh cross section area (a) image of acetylene black mesh, (b) maps of sulfur and (c) carbon in acetylene black mesh after cycling

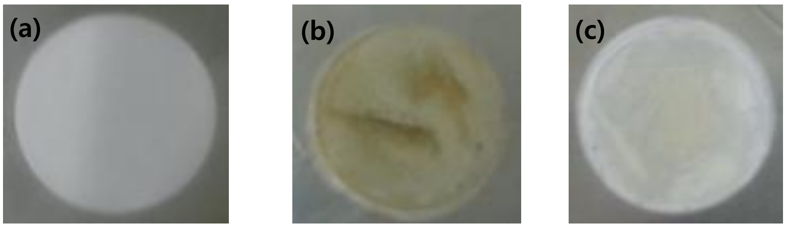

Figure S4. Appearance of the separator : (a) original separator, (b) without and (c) with acetylene black mesh after cycling.

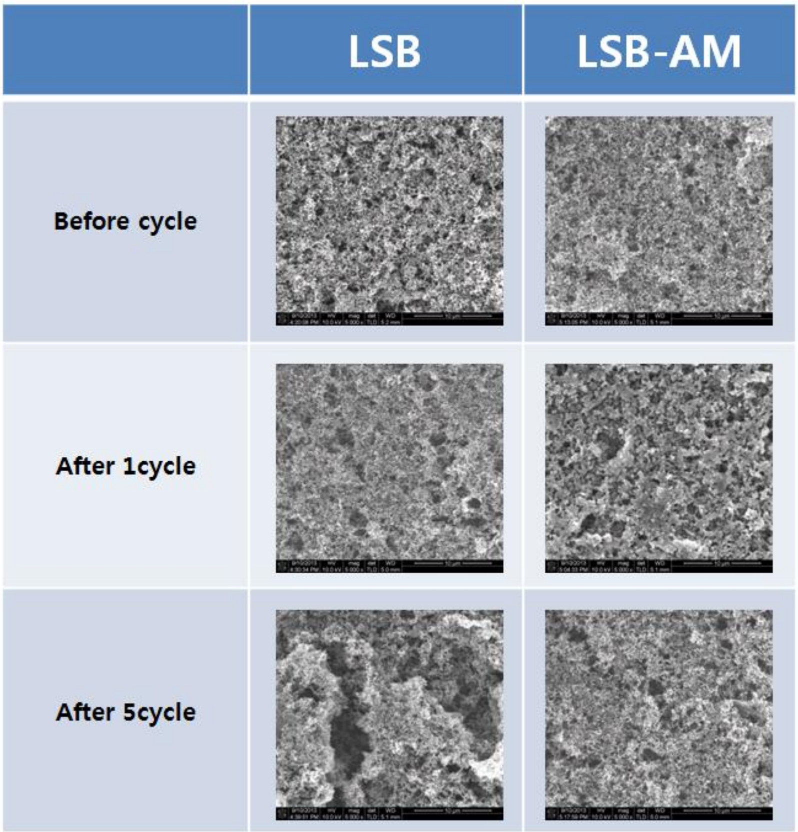

Figure S5. SEM images demonstrating the surface morphology change in the cathode with charge/discharge cycles

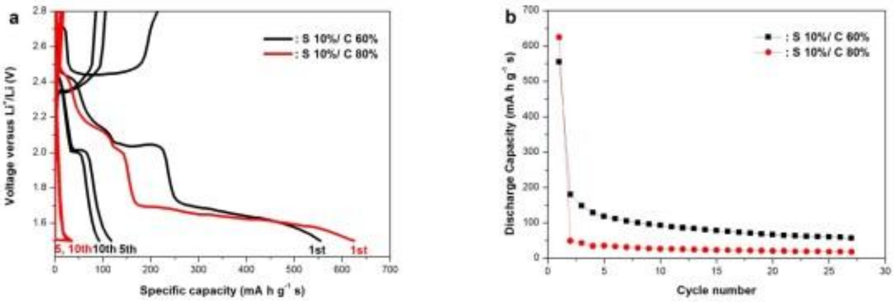

Figure S6. Electrochemical performance of sulfur/carbon composite cathode as different carbon content. (a) voltage profiles and (b) cycle performances of sulfur/carbon composite cathode having high content of carbon (60 or 80% of carbon).