Supporting Information

Reactivation of Dissolved Polysulfides in Li-S Batteries Based on Atomic Layer Deposition of Al_2O_3 in Nanoporous Carbon Cloth

Xiaogang Han[1], Yunhua Xu[2], Xinyi Chen[1], Yu-Chen Chen[1], Nicholas Weadock[1], Jiayu Wan[1], Hongli Zhu[1], Yonglin Liu[1], Heqin Li[1], Gary Rubloff[1], Chunsheng Wang[2], Liangbing Hu[1,*]

[1]Department of Materials Science and Engineering, [2]Department of Chemical Engineering, University of Maryland, College Park, Maryland 20742, United States

*Corresponding author. Tel.: +1 301 405 9303; Fax: +1 301 314 8514. E-mail address: binghu@umd.edu

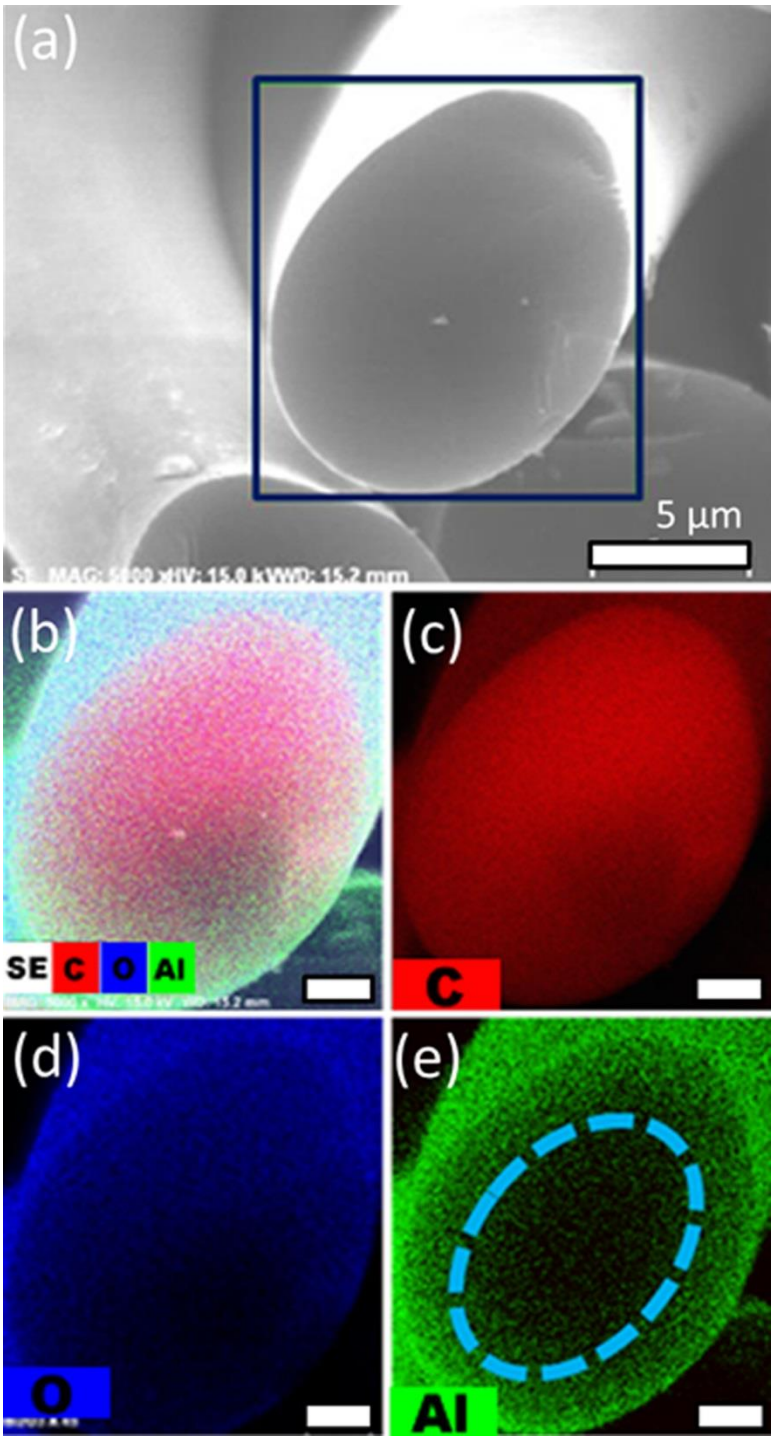


Figure S1. Cross-section SEM/EDS micrographs of ALD Al_2O_3 coated ACC fibers (Al_2O_3-ACC). (a) is the SEM image, (b) is the overlap of element mapping and SEM image, and (c-e) are the separate elemental maps for C, O, and Al, respectively. The dotted blue circle marks the boundary of Al distribution. The scale bars in (b-e) are 2 µm.

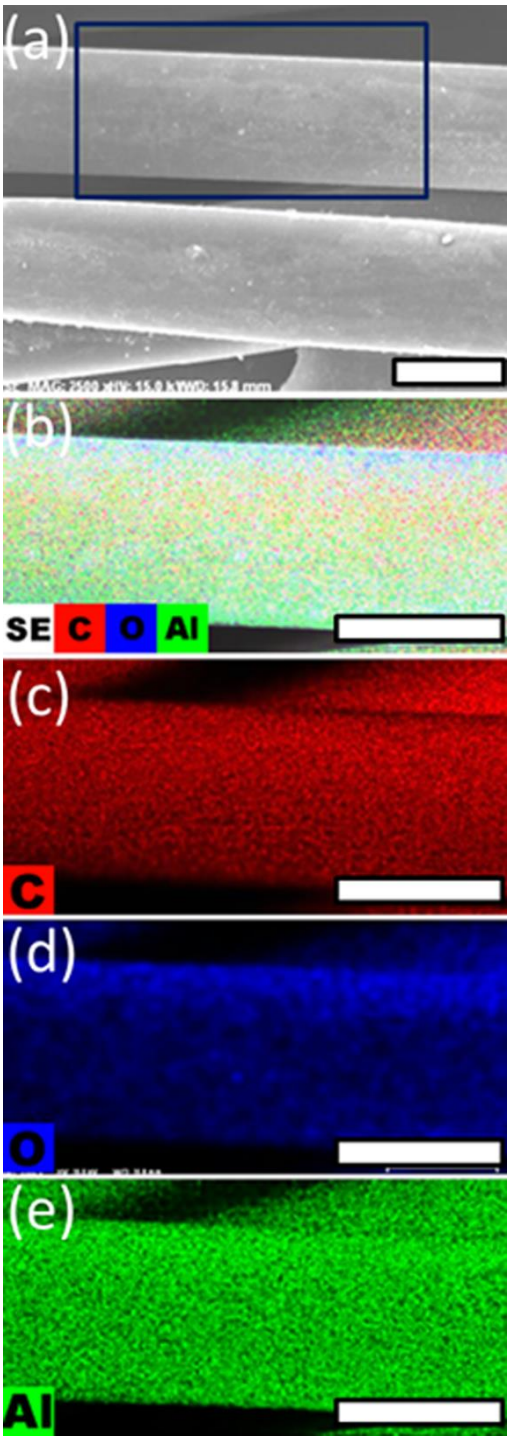


Figure S2. SEM/EDS of the side-wall surfaces of Al_2O_3-ACC: (a) SEM image, (b) overlap of elemental maps and SEM image, and (c-e) the separate elemental maps for C, O, and Al, respectively. All scale bars are 7 μm.

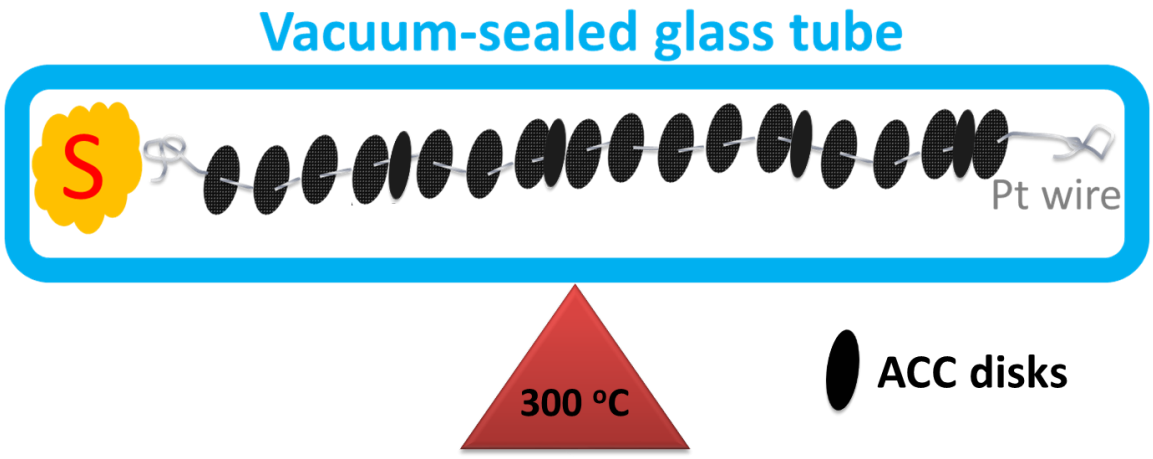


Figure S3: Schematic of the setup for the sulfur infiltration in ACC disks using vacuum-sealed glass tube. The Pt wire transpiercing all the ACC disks aids in disk sample identification. The infiltration is performed at 300 ºC followed by cooling down in 24 hours (see the Experimental Section).

The C:S mass ratio or S loading amount is important for battery performance evaluation, and a simple method to get the mass ratio is TGA operated with flowing nitrogen or argon. Unfortunately, we could not find an available TGA around. The volatilized sulfur created during the thermal process in inert gas was believed to leave residue and contaminate the instrument. As such, we employed a calculation method for sulfur content in the manuscript. Simply put, the sulfur mass was obtained from the mass increase of the ACC disk after sulfur loading, *i.e.* by precisely measuring the ACC disk before and after the sulfur infiltration with a microbalance (Resolution of 1 μg, Sartorius ME5, Data Weighing Systems, Inc.) Figure S3 schematically illustrates the approach. The punched ACC disks (ϕ 1/4″, 20 pieces) were measured and numbered, transpierced with a platinum (Pt) wire for identification and then put in a glass tube (ϕ 1/2″). After adding a measured amount of sulfur the glass tube was vacuum-sealed and heated at 300 ºC in an oven for sulfur infiltration. The mass ratio of sulfur powder to all ACC disks was set at 1.5.

After the infiltration, each ACC disk was massed again and the mass increase calculated to determine the mass of sulfur loading for each corresponding ACC disk. As shown in Table S1, the average sulfur loading amount per disk is 3.74 mg, and the average ratio of S:C is 1.45 for every disk, which is very close to the designed ratio of 1.5. The sulfur content in the S-loading layer is 59.2%.

Table S1: Calculation of sulfur loading amount from mass increase

Sample	Mass/mg			S%****
	C*	C+S**	S***	
1	2.577	6.335	3.758	59.3%
2	2.519	6.228	3.709	59.6%
3	2.624	6.434	3.81	59.2%
4	2.587	6.365	3.778	59.4%
5	2.63	6.305	3.675	58.3%
6	2.528	6.215	3.687	59.3%
7	2.61	6.406	3.796	59.3%
8	2.608	6.395	3.787	59.2%
9	2.635	6.449	3.814	59.1%
10	2.631	6.444	3.813	59.2%
11	2.55	6.277	3.727	59.4%
12	2.473	6.099	3.626	59.5%
13	2.507	6.186	3.679	59.5%
14	2.774	6.732	3.958	58.8%
15	2.414	5.975	3.561	59.6%
16	2.47	6.094	3.624	59.5%
17	2.653	6.452	3.799	58.9%
18	2.549	6.267	3.718	59.3%
19	2.625	6.417	3.792	59.1%
20	2.465	6.055	3.59	59.3%
Average	2.571	6.307	3.735	59.2%
			STD	0.3%

* The mass of sulfur loaded ACC disks

** The mass of sulfur loaded ACC disks after removal of sulfur by heating in Ar/H_2 (5%, v/v)

*** The mass of sulfur calculated from the difference of C+S and C

**** S% = S/(C+S) X 100%

To check the validity of the above method, we designed a pseudo TGA method to calculate the sulfur loading amount, which, like TGA, is based on mass decrease. Briefly,

the sulfur loaded ACC was heated at 600 ºC in tube furnace flowing Ar/H_2 (5%, v/v) to remove the sulfur and then the ACC massed again. In this method the hydrogen reacts with S at high temperatures forming H_2S gas, facilitating the removal of S. Table S2 presents the results. The average sulfur loading amount per disk is 3.68 mg, the average ratio of S:C 1.43, and sulfur content in the S-loading layer 58.8%, all of which are nearly identical to those calculated from the previous method. It is implied that the infiltrated sulfur does not react with carbon and exists as elemental sulfur, agreeable with the typical sulfur properties in the electrochemical characterization tests. Figure S4 is a comparison of sulfur loading amounts calculated from mass increase and decrease methods. Clearly, the two groups of values have no notable differences. The validity of calculated sulfur mass is thus confirmed.

Table S2: Calculation of sulfur loading amount from mass decrease

Sample	Mass/mg			S%****
	C+S*	C**	S***	
1	6.311	2.578	3.733	59.2%
2	5.556	2.356	3.200	57.6%
3	6.222	2.578	3.644	58.6%
4	6.133	2.533	3.600	58.7%
5	6.533	2.667	3.867	59.2%
6	6.444	2.622	3.822	59.3%
7	6.533	2.667	3.867	59.2%
Average	6.248	2.571	3.676	58.8%
			STD	0.6%

* The mass of sulfur loaded ACC disks

** The mass of sulfur loaded ACC disks after removal of sulfur by heating in Ar/H_2(5%, v/v)

*** The mass of sulfur calculated from the difference of C+S and C

**** S% = S/(C+S) X 100%

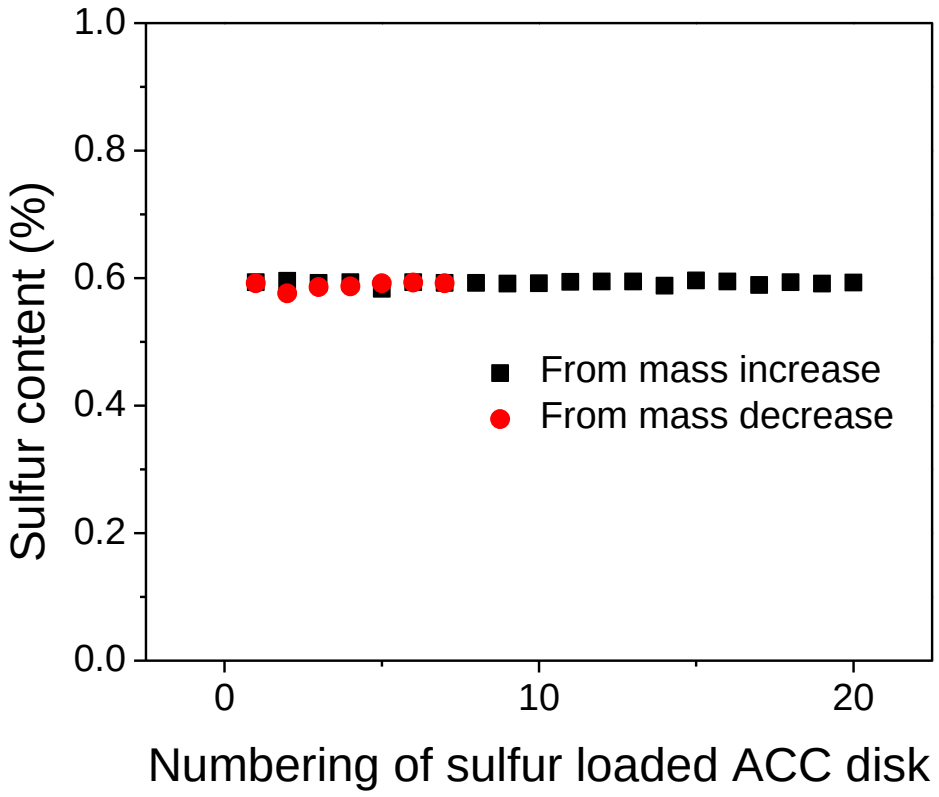


Figure S4: Plot of S/C mass ratio in each ACC disk in the same batch for sulfur infiltration by mass increase (black) /decrease (red) method.

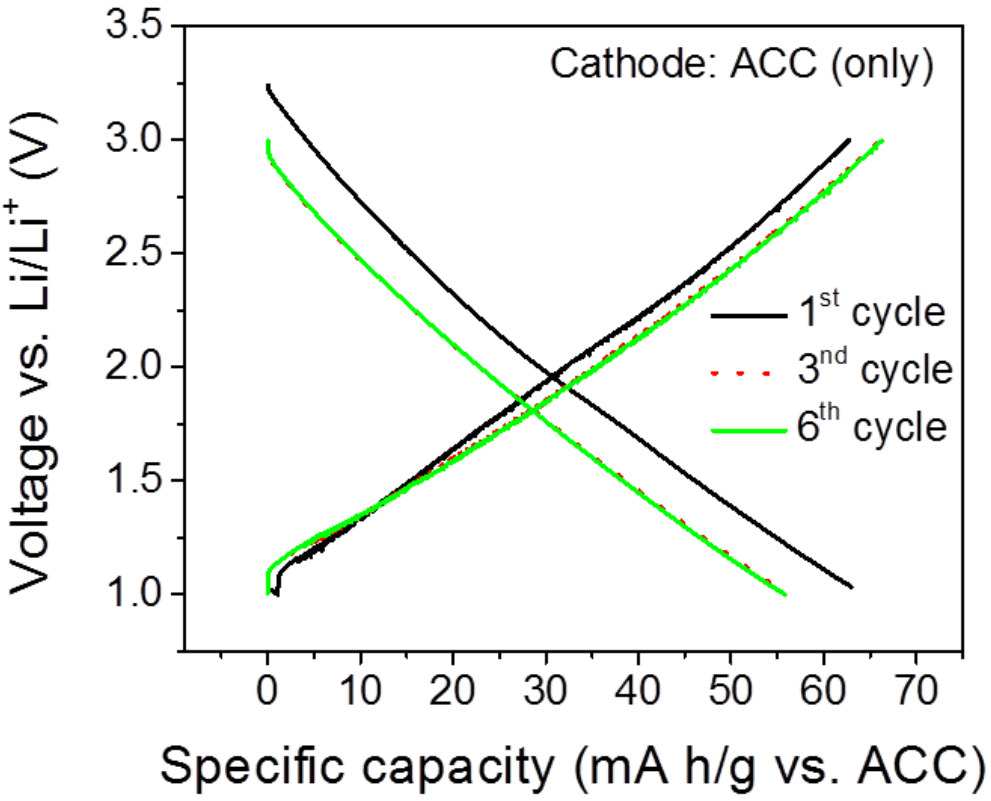


Figure S5. The galvanostatic discharge/charge profile of the bare ACC cathode for the control tests at a current density of 11.8 mA/g.

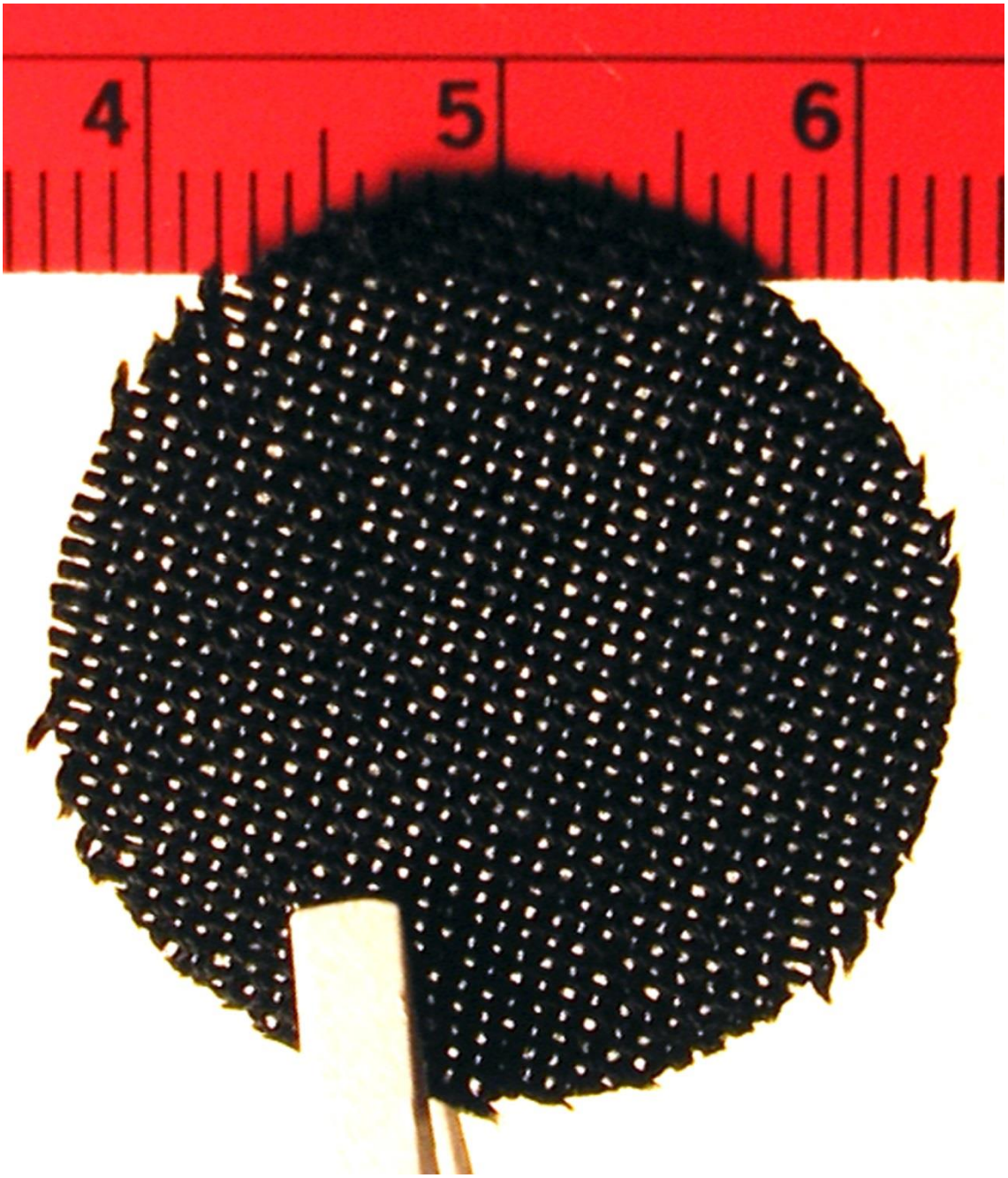


Figure S6. Digital photo of ACC showing large gaps between the bundles of active carbon fibers. Each gap is several hundred micrometers across. The unit of the ruler is cm.

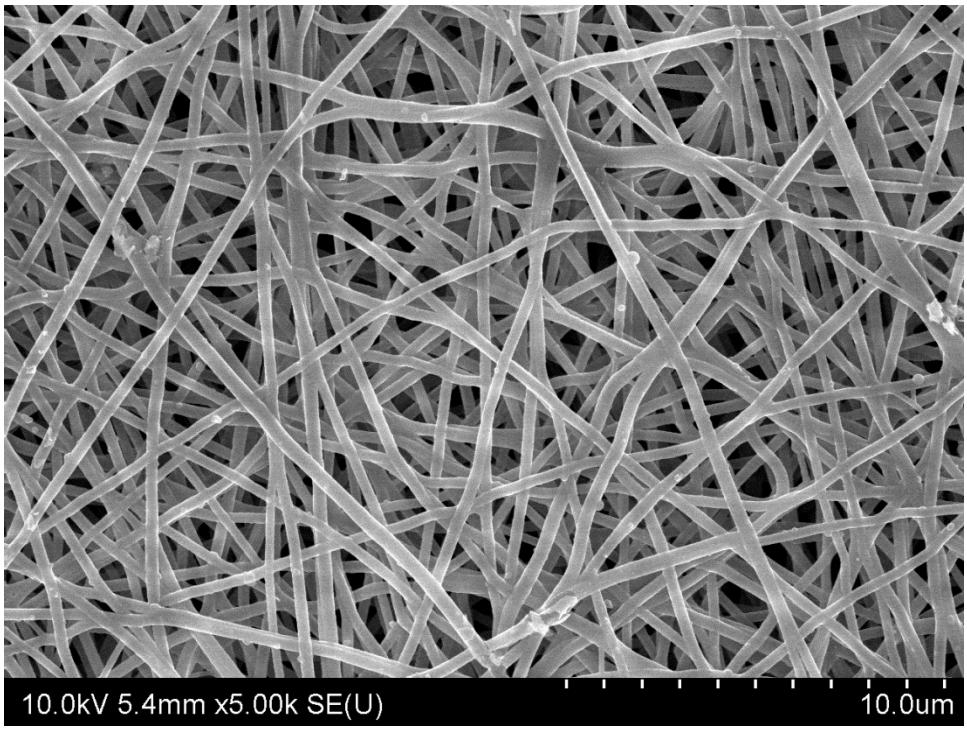


Figure S7: SEM image of an electrospun fiber film with ALD-Al_2O_3 and carbon coating. The film shows a much higher fiber density and smaller fiber size comparing with the carbon cloth.