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#### **Experimental**

Unless otherwise noted, all procedures were carried out in the fume hood. All reagents were commercially available and used without further purification. Zeta potential and size distribution of particles were measured on a Zetasizer nano range (Malvern). The shape of materials was observed by field emission scanning electron microscopy (FE-SEM) on a JSM-7800F (JEOL). Preparation of cross-section of particle was conducted by a focused ion beam with gallium ion beam at -100 °C on a FB-2100 (HITACHI High-Tech). Thickness of the layer by layer membranes built on silicon wafer substrate was measured on an ellipsometer, LSE (Gaertner).

#### Functionalization of conductive carbon

Ketjen Black® (1.25 g, ECP 600jd, LION) was put in a 1 L conical flask with deionized water (250 mL) and nitric acid (250 mL, HNO<sub>3</sub>, 70 %, Sigma-Aldrich), and rapidly stirred for three days at 70 °C. After three days, the acid treated carbon was separated from acidic solution by centrifugation at 12000 rpm for 1 minute. (Caution should be taken during this step.) This treated carbon was rinsed with distilled water at least 5 times until the separation of carbon become difficult. The degree of functionalization of carbon in  $H_2O$  was examined by Zeta potential. After the rinsing, the zeta potential of functionalized carbon showed -48 mV.

### One step synthesis of sulfur particles embedded with nanocarbon coated with poly(3,4ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS)

Sodium thiosulfate (50 g, 0.316 mol, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, 99 %, Reagent Plus®, Sigma-Aldrich) was dissolved in deionized water (1.5 L) in a 4 L beaker. PEDOT:PSS (35 mL, 1.1 % in H<sub>2</sub>O, high conductive grade, Sigma-Aldrich) was added to the sodium thiosulfate solution and stirred. Oxalic acid (157 g, 1.90 mol, (COOH)<sub>2</sub>, >99.0 %, Sigma-Aldrich) was dissolved in deionized water (2.44 L) in a 4 L beaker. The mole ratio of sodium thiosulfate and oxalic acid was 1:6. The functionalized carbon (60 mL, 3 mg in 1 mL of distilled water) was dispersed in the oxalic acid solution. This acidic solution was poured quickly into the sodium thiosulfate solution, and the solution color turned creamy gray. The solution was stirred rapidly at room temperature. After 3 hours, this solution was sonicated for 5 minutes. The precipitated sulfur particles were obtained by centrifugation at 3000 rpm for 5 minutes. The sulfur particles. The rinsing process should be done thoroughly and this rinsing procedure was repeated for 5 times.

# Assembling of the Nafion® based PEML membranes comprising of poly(diallyldimethylammonium chloride) (PDADMAC) and Nafion®

The PEML membranes were assembled by sequential adsorption of oppositely charged polyelectrolyte on sulfur particles embedded nanocarbon coated with PEDOT:PSS polyelectrolyte (5 g). The first layer (PDADMAC) was built on the negatively charged sulfur particles embedded nanocarbon coated with PEDOT:PSS. Lithium nitrate (6.9 g, 0.1 mol) was

dissolved in deionized water (1 L). In a 1 L conical flask, the PDADMAC (6 mL, 0.0074 mmol, 20 wt.% in H<sub>2</sub>O, average Mw 200,000-350,000, Sigma-Aldrich) was dissolved in the 0.1 M LiNO<sub>3</sub> solution (1 L) and stirred. After 5 minutes, sulfur particles coated with PEDOT:PSS were dispersed into this positively charged polymer solution and stirred for 1 hour. The polymer adsorbed particles were obtained by centrifugation. These particles were rinsed with 0.1 M LiNO<sub>3</sub> solution by vortex at 3000 rpm for 30 seconds and centrifuged again. After 3 times rinsing, negatively charged polyelectrolyte (Nafion®) was adsorbed as the second layer on the particles through the almost same procedure above. The Nafion® solution (6 ml, 0.0006 mmol, 5 wt. % in mixture of lower aliphatic alcohols and water, contains 45% water, Sigma-Aldrich) was dissolved in 0.1 M LiNO<sub>3</sub> ethanol water (1 L, 50 % ethanol). The particles were stirred in this solution for 1 hour and rinsed with 0.1 M LiNO<sub>3</sub> ethanol water. Then, the same procedure was repeated sequentially until the fifth layer (PDADMAC). The observation of building PEML membranes was carried out by the zeta potential analysis. The switching of the zeta potential on the surface which corresponded the charging of adsorbing polymer was observed sequentially.

## Assembling of the PEDOT:PSS based PEML membranes comprising of PDADMAC and PEDOT:PSS

The PEML membranes were built on sulfur particles embedded nanocarbon wrapping with PEDOT:PSS polyelectrolyte (5 g) as described above, substituting Nafion® for PEDOT:PSS. At this point, PEDOT:PSS (6 ml) was dissolved in 0.1 M LiNO<sub>3</sub> solution (1 L).

### Assembling of the Nafion® based PEML membranes with branched polyethylenimine (B-PEI) as second layer

The PEML membranes were built on sulfur particles embedded nanocarbon wrapping with PEDOT:PSS polyelectrolyte (5 g) as described above, substituting PDADMAC for B-PEI as the first layer. At this point, B-PEI (3 mg, 99 % in H<sub>2</sub>O, Mw 10,000, Alfa Aesar) was dissolved in 0.1 M LiNO<sub>3</sub> solution (1 L). In addition, the second step and the third step were repeated sequentially until the seventh layer (PDADMAC).

# Decorating functionalized carbon on the top of the PEML membranes encapsulating sulfur particles

The functionalized carbon which has negative charge was adsorbed on the top of the positively charged surface of the sulfur particle encapsulated with the PEML membranes. The functionalized carbon (20 mg) was dispersed in deionized water (1 L) in a 1 L conical flask. Then, the sulfur particles were put into this solution and stirred for 4 hours. After 4 hours reaction, the particles were separated by centrifuging from the solution. If functionalized carbon is adsorbed on sulfur particle well, a clear supernatant should be observed. At the last step, the particles were dried at 80 °C for 12 hours.

## Building PEML membranes consisting of B-PEI, Nafion® and PDADMAC on the silicon wafer

B-PEI which has positive charge was used as the first layer. Lithium nitrate (6.9 g, 0.1 mol, LiNO<sub>3</sub>, 99.9 %, Sigma-Aldrich) was dissolved in deionized water (1 L). Then the B-PEI (2.36 g) was dissolve in the 0.1 M LiNO<sub>3</sub> solution (100 mL) in a 140 mL beaker. Three 140 mL beakers of 0.1 M LiNO<sub>3</sub> solution (100 mL) were prepared for rinsing. A silicon wafer (2.54 cm diameter, single side polished, Virginia Semiconductor) was hold by tweezers and dipped into the B-PEI solution for 10 minutes. After the adsorption process, the wafer was dipped in 0.1 M LiNO<sub>3</sub> solution and rinsed for 1 minute. This rinsing process was repeated two times while changing the solution following drying process with nitrogen gas for 30 seconds. During adsorption and rinsing, the solution was stirred. The Nafion® which has negative charge was adsorbed as the second layer. The Nafion® (54.4 g) was dissolved in 0.1 M LiNO<sub>3</sub> ethanol water (100 mL, 50 % ethanol) in order to the Nafion® was dispersed well. Also, three beakers of 0.1 M LiNO<sub>3</sub> ethanol water (100 mL). The adsorption process and the rinsing process were conducted as described above. The third layer was the positively charged PDADMAC. The PDADMAC (4.04 g) was dissolve in the 0.1 M LiNO<sub>3</sub> solution (100 mL). Then the silicon wafer was dipped into the PDADMAC solution for 10 minutes and rinsed three times as explained above. The adsorption process of Nafion® and PDAMAC can be repeated such that any desired number of layers can be adsorbed. Thickness of layer by layer membranes were measured each step by an ellipsometer.

#### **Cathode preparation**

Sulfur cathode sheet was formed by using doctor blade method on the top of aluminum foil (14 µm of thickness). Cathode slurry was consisted of the active material, conductive carbon powder, and polymer binder dispersed in deionized water. The active material (0.5 g), carbon nanofiber (133.9 mg, CNF, Sigma-Aldrich), and Ketjen Black® (44.7 mg) were put in a 45 ml zirconia container with zirconia balls (40 g, 3 mm diameter). This mixture was ball milled at 120 rpm for 1 hour. After an hour, this active material-carbon mixture was taken out from the container and mixed with carboxymethyl-cellulose solution (793 µL, 3 wt.%, CMC, dispersed in deionized water, MTI) and styrene-butadiene rubber solution (297.5 µL, 4 wt.%, SBR, dispersed in deionized water, MTI) in a mortar by using a pestle for 10 minutes. This slurry was kneaded in a planetary centrifugal mixer (ARE-310, THINKY) at 2000 rpm for 3 minutes following deformed process at 2200 rpm for 30 seconds. During this process, viscosity of the slurry was adjusted by adding extra deionized water (up to 1 mL). After aluminum foil was defatted with acetone, cathode slurry was coated on the aluminum foil with doctor blade. The gap of the blade was adjusted properly to demands of sulfur areal loading; i.e. the gap of 50 µm was used to make 1 mg/cm<sup>2</sup> cathode, the gap of 170 μm was used to make 3 mg/cm<sup>2</sup> cathode, the gap of 300 μm was used to make 5 mg/cm<sup>2</sup> cathode and the gap of 480  $\mu$ m was used to make 9 mg/cm<sup>2</sup> cathode. Coated cathode film was dried at 80 °C in drying furnace for 6 hours. This cathode sheet was cut to 19 mm diameter disk.

#### **Electrochemical characterization**

Battery testing was conducted in a 2032 stainless coin type cell using DOL:DME (1:1, v/v) with 1 M LiTFSI and 0.2 M LiNO<sub>3</sub> electrolyte. The amount of electrolyte was approximately 40 µL. The Celgard® 2325 or the cotton disk was used as separator; the Celgard® was used for low areal loading cathode and the cotton separator was used for high areal loading cathode. Lithium metal disk was used as anode. The battery performance was evaluated by galvanostatic cycling at 25 °C. Charge and discharge rates were calculated assuming theoretical capacity for the total amount of sulfur in cathode. BioLogic SAS, model VMP3, multi-channel Science Instruments potentiostats were used for electrochemical measurements. Data were processed with EC-Lab Software V10.35 with the corresponding VMP3 firmware, provided by Science Instruments.



**Fig. S1** (A) Comparison of size distribution of sulfur particles embedded with Ketjen Black® coated with PEDOT:PSS synthesized in presence of oxalic acid (red ) or hydrochloric acid (black). (B) Typical SEM image of sulfur particles synthesized in presence of oxalic acid.



**Fig. S2** Typical SEM images of sulfur particles embedded with nanocarbon coated with PEDOT:PSS.



**Fig. S3** Typical SEM images of sulfur particles embedded with nanocarbon coated with (A) PVP, (B) PPy and (C) PDADMAC.



**Fig. S4** (A) Qualitative SEM/EDX analysis of sulfur particles embedded with nanocarbon and coated with PEDOT:PSS. (B) Thermogravimetric analysis of sulfur particles embedded with nanocarbon and coated with PEDOT:PSS.



**Fig. S5** Cycling stability of Li-S batteries with sulfur particles encapsulated with Nafion® based membranes. Areal sulfur loading was 3 mg/cm<sup>2</sup>. Operating rate of 0.1 C.