

## Vertically-Aligned Carbon Nanotubes on Aluminum as a Light-Weight Positive Electrode for Lithium-Polysulfide Batteries

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### Experimental section

*Fabrication of VACNTs on aluminum:* Vertically aligned carbon nanotubes were synthesized using a catalyst supported chemical vapor deposition technique. The 20 µm-thick aluminum substrate (Sumikei Al, Japan) was cleaned thoroughly by sonication in acetone and isopropanol baths, and by a plasma treatment (O<sub>2</sub> 0.1 mbar, 100 W, 2 min). A thin layer of iron catalyst (0.5 nm) was deposited on the clean aluminum substrate using an electron beam physical vapor deposition (EBPVD) technique. The growth of CNT arrays was performed at low pressure (around 1 mbar), in a vertical hot-wall Plassys® CVD reactor equipped with an array of 10 conductive filaments connected to a power source. For the highest nanotube arrays obtained, the growth was conducted as follows: acetylene (C<sub>2</sub>H<sub>2</sub>, 20 sccm), the carbon precursor, was introduced in the reactor diluted in hydrogen (H<sub>2</sub>, 50 sccm) and helium (110 sccm), for a total pressure of 1.2 mbar. The filaments were switched on and the power was increased to 700 W. The chamber was heated up to 450 °C thanks to additional heat sources. The system reached 450 °C after 12 min, and the temperature was sustained for 30 min. For shorter nanotube arrays, the duration of the plateau at high temperature was reduced. Images of the electrodes structure before and after cycling, and element mapping using electron dispersive X-ray spectroscopy, were realized within a Zeiss LEO 1530 scanning electron microscope. CNT structure and diameter was characterized by transmission electron microscopy (FEI Tecnai Osiris operating at an acceleration voltage of 200 kV). Specific

surface area analyses were performed on VACNT samples using BET method (Micromeritics, Tristar II 3020).

*Catholyte preparation:* Sulfur was introduced in the batteries in the form of polysulfides (of average formula  $\text{Li}_2\text{S}_6$ ) dissolved in the electrolyte, proceeding as follows. In an argon-filled glove box, metallic lithium cut into small pieces and sulfur powder (99.5%, 325 mesh, Alfa Aesar) were introduced in a 9:1 vol. mix of 1,2-dimethoxyethane (DME, anhydrous, 99.5%, Aldrich) and 1,3-dioxolane (Diox, anhydrous, 99.8%, Aldrich) in the proper stoichiometry to yield  $\text{Li}_2\text{S}_6$  0.25 M. Lithium bis(trifluoromethane sulfone)imide (LiTFSI, 99.95%, Aldrich) and lithium nitrate ( $\text{LiNO}_3$ , 99.99%, Aldrich) were dissolved to 1 M and 0.1 M respectively.<sup>1</sup> At least 48h of stirring at 50°C were necessary to dissolve all of the solid compounds.

*Electrochemical characterization:* The VACNT structures obtained on aluminum were punched to 14 mm diameter electrodes and then used directly as positive electrodes in CR2032 coin cells. No sulfur deposition was performed since the positive active material was introduced with the electrolyte. The Li/polysulfide coin cells were assembled in an argon-filled glove box and tested in a galvanostatic mode between 1.8 and 3 V vs.  $\text{Li}/\text{Li}^+$ . A metallic lithium disk (16 mm) was used as a negative electrode. A Celgard 2400<sup>®</sup> served as the separator, assisted by a non-woven Viledon<sup>®</sup> layer to provide an electrolyte reservoir. 75  $\mu\text{L}$  of catholyte was used in the coin cells, which contained 3.6 mg of sulfur. The theoretical loading was 3.9  $\text{mAh cm}^{-2}$  and the sulfur to electrolyte ratio was 48  $\text{mg mL}^{-1}$ . For the comparison, a commercial carbon paper from Freudenberg (GDL-H2315<sup>®</sup>) was selected,<sup>2</sup> and evaluated in the same conditions as VACNT. A reference composite electrode was also prepared, consisting of 80% sulfur (99.5%, 325 mesh, Alfa Aesar), 10% Super P<sup>®</sup> (Timcal) and 10% poly(vinylidene fluoride) (PVdF 1015, Solvay) on an aluminum foil. In this case, the electrode loading was 3.2  $\text{mAh cm}^{-2}$ .

## References

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- 2 C. Barchasz, F. Mesguich, J. Dijon, J.-C. Leprêtre, S. Patoux, F. Alloin, *J. Power Sources*, 2012, **211**, 19.