Supplementary Information

Printed Microelectrodes for Scalable, High-areal-capacity Lithium-sulfur Batteries

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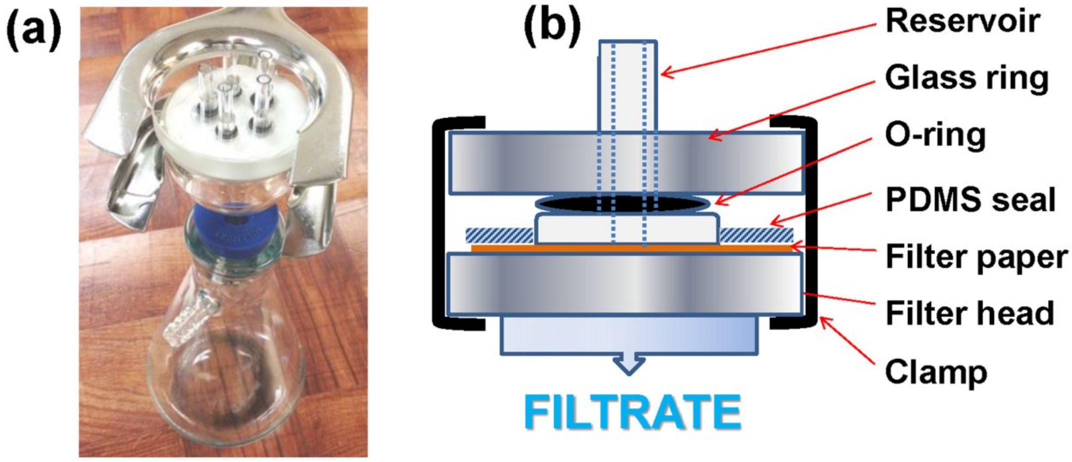
Experimental Section

Materials and Printed Electrode Preparation: All materials were used as received, without further purification or modification. MWCNT printing inks were prepared by adding 75 mg of aligned multiwall carbon nanotubes (aMWCNT, US Research Nanomaterials, stock # US4522) to 300 mL of de-ionized water and 30 mL of isopropyl alcohol (for improved MWCNT wetting), followed by bath sonication for 60 min, probe ultrasonication for 15 min (Sonics Vibra-cell; 3s on, 1s off, 30% amplitude), and bath sonication for another 15 min. Effective separation of aMWCNT bundles during sonication was found to be essential for producing stable inks (*i.e.* no observable macro-bundling or settling over ~ 1 – 5 days) and high-performance printed electrodes. The freestanding MWCNT microelectrodes were fabricated by printing the inks with a Nordson EFD Ultimus IV high-precision fluid dispenser (10 cc barrel, white O 10 cc piston / wiper 30, and 20 gauge TT 0.023” pink 50 PC tip) through a glass reservoir assembly (Figure S1) consisting of glass tubes (Simax borosilicate tubing, 3.0 nominal inner diameter) with flanged bases (produced via heat-treatment with a graphite rod held inside the tube to preserve the nominal inner diameter) that were held flush to the 47 mm nylon membrane filter (0.8 μm pore size, Whatman, GE Healthcare Lifesciences) with O-rings and a borosilicate glass disk (McMaster-Carr) to produce the desired electrode diameter of ~ 3.1 mm (Figure 1e). Masks made from polydimethylsiloxane (PDMS, Sylgard 184, Dow Corning) films approximately 1 mm thick were used to cover the entire nylon membrane filter (except the areas in contact with the bases of the glass reservoirs) for improved vacuum during filtration. The entire assembly was secured to a standard ceramic filter head with a custom DELRIN® (DuPont) horseshoe clamp (Figure S1). After printing, the electrodes were rinsed with de-ionized water, ethanol, and acetone. Immediately after rinsing, the filtration apparatus was disassembled and the electrodes were extracted by carefully flexing the filter. The electrodes were then dried for 24 - 48 h at 50 °C in a vacuum-oven to remove residual solvent. A Nikon SMZ1500 optical microscope was used to measure the final diameter. We also prepared inks using surfactants such as sodium cholate (0.1% wt/vol., Sigma-Aldrich) and TRITON 45-X (Acros); however, we observed that the capacity of the electrodes made with surfactant-containing inks was significantly lower than those prepared with surfactant-free inks, probably due to electrode surface poisoning from residual surfactant not removed by rinsing.

Active Material Synthesis: To prepare blank electrolyte, we dissolved lithium trifluoromethanesulfonate ($LiCF_3SO_3$, 98 %, Sigma-Aldrich) and lithium nitrate ($LiNO_3$, 99 %, Acros Organics) in a mixture of dimethoxy ethane (DME, 99 %, Sigma-Aldrich) and 1,3-dioxolane (DOL, 99.5+ %, Acros Organics) (1:1 v/v) to generate 1 M $LiCF_3SO_3$ and 0.1 M $LiNO_3$. Stoichiometric amounts of sublimed sulfur powder (99.5 %, Acros) and lithium sulfide (Li_2S, 99.9 %, Acros) were added to the blank electrolyte to synthesize dissolved polysulfide catholyte solutions (0.67 M Li_2S_6, equivalent to 4 M sulfur). The solutions were heated at 45 - 50 °C in an Ar-filled glove box for 18 h to produce the dark orange/brown Li_2S_6 catholyte.

Coin Cell Assembly: Dissolved lithium polysulfide cells were assembled in an Ar-filled glove box by placing the freestanding printed electrodes inside a cathode cell cap, then adding 2 or 4 μL polysulfide catholyte to give, respectively, dosages of 0.256 mg sulfur (*i.e.*, 3.4 mg cm^{-2}) or 0.512 mg sulfur (*i.e.*, 6.8 mg cm^{-2}). In sequence, a Celgard 2500 separator, blank electrolyte, and a lithium-metal anode were added on top of the MWCNT cathode, and the CR2032 coin cells were sealed with an electrode press prior to removal from the glovebox for cycle testing. The ratio of electrolyte to sulfur, in terms of "active" electrolyte (*i.e.* polysulfide solution), was 7.8 μL mg^{-1} S for both 3.4 mg cm^{-2} and 6.8 mg cm^{-2}, and the estimated ratio of total electrolyte to sulfur was approximately ~ 40 μL mg^{-1} and ~ 25 μL mg^{-1}, respectively, for 3.4 mg cm^{-2} and 6.8 mg cm^{-2} dosages.

Electrode Analysis and Electrochemical Measurements: Physical morphology was evaluated with a Zeiss SUPRA 40 VP or FEI Quanta 650 scanning electron microscope (SEM) and NIKON SMZ1500 optical microscope. Elemental mapping was realized using an energy dispersive spectrometer (EDS) attached to the FEI Quanta 650 SEM. XRD data were collected at $2\theta = 10 – 70^{o}$ on a Philips X-ray diffractometer equipped with CuKα radiation in steps of 0.02°. Cycled MWCNT electrodes were opened inside the glovebox, soaked in DME for 10 min, dried, and mounted for XRD and SEM / EDS measurements. Cyclic voltammagrams were generated on a VoltaLab PGZ402 between 1.8 and 2.8 V at a scan rate of 0.05 mV s^{-1}. An Arbin battery test cycler was used to galvanostatically test coin cells between 1.8 and 3.0 V at C/2 and 1C rates.



(c) Filtration assembly

(d) Printed electrodes

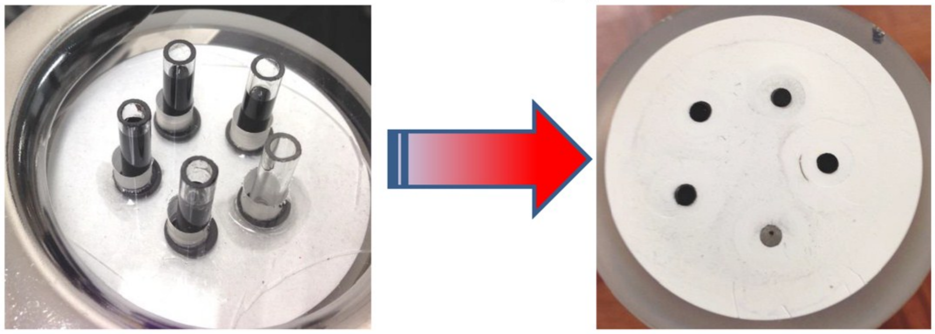


Figure S1: (a) Glass reservoir filtration assembly used to fabricate printed electrodes, (b) schematic of the assembly, comprising: custom-made glass reservoir stems to direct the filtration of MWCNT to isolated sections of the membrane filter; a glass ring, O-ring, and custom-built clamp to secure the glass reservoirs to the filter; and a PDMS seal to improve suction; top-view images of (c) the assembly during filtration, and (d) the as-fabricated electrodes on the filter immediately after printing, with one electrode removed to demonstrate the clean extraction that was achieved.

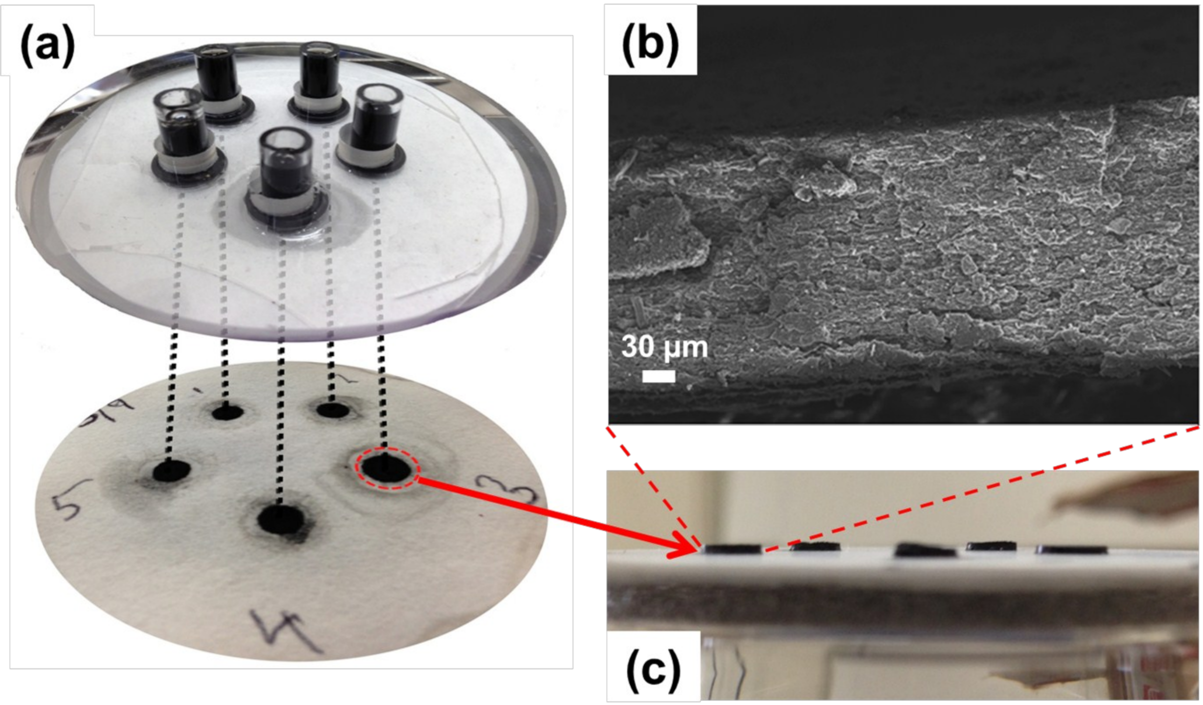


Figure S2: Schematic showing (a) the printing assembly, (b) a cross-sectional SEM image and (c) optical image of ultra-thick printed electrodes on the filter immediately after printing, demonstrating the robust stability of printed electrodes.

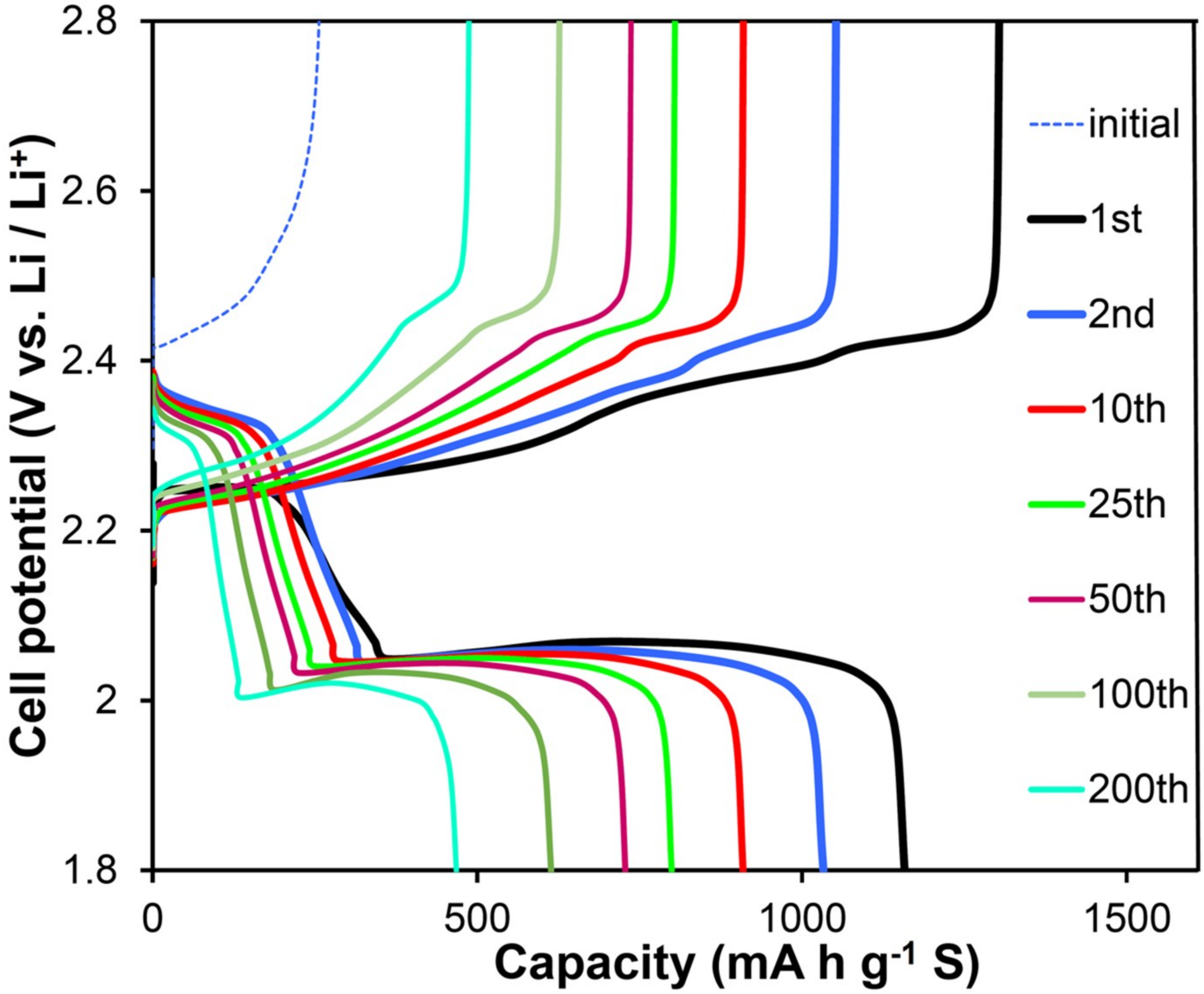


Figure S3: Voltage profiles of the galvanostatic charge-discharge cycling of a cell with 6.8 mg cm^{-2} sulfur loading and cycled at C/2 rate. Electrode polarization is low, but electropassivation is evident after ~ 100 cycles compared to the cell with 3.4 mg cm^{-2} sulfur loading cycled at C/2 rate (Figure 3b), which did not display electropassivation.

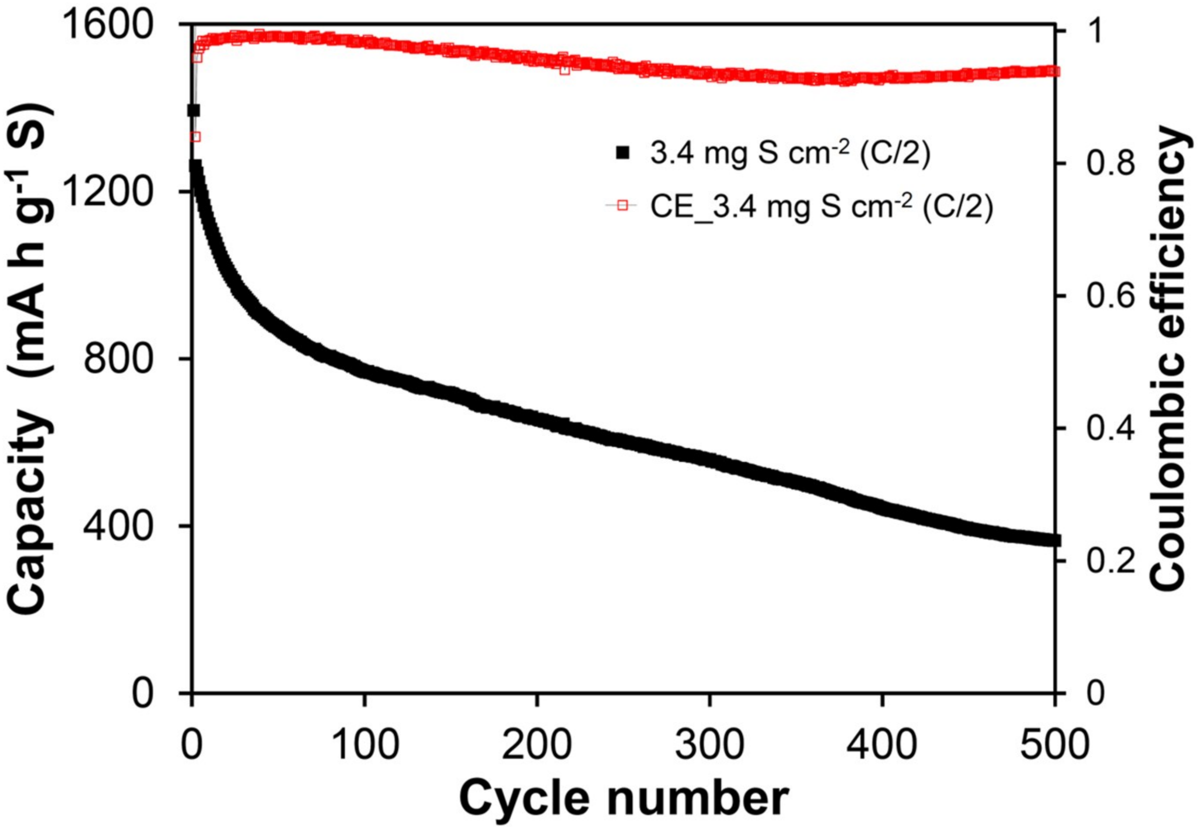


Figure S4: Extended galvanostatic cycle performance for a cell with 3.4 mg cm^{-2} sulfur loading and C/2 rate. The observed rate of capacity fade is nearly constant after ~ 25 cycles.

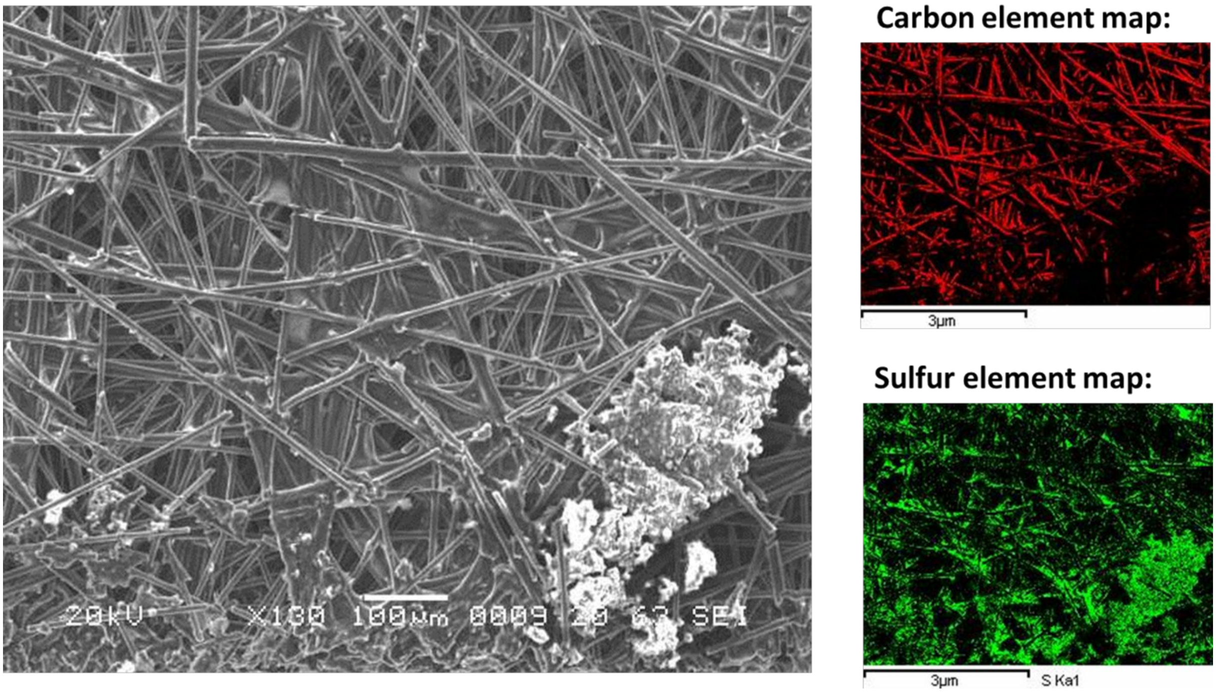


Figure S5: SEM image of commercial TORAY carbon fiber paper after 100 cycles (left), and EDS elemental maps for carbon (upper right) and sulfur (lower right) that clearly show large, electrochemically isolated, solid sulfur species deposited on the surface due to inefficient

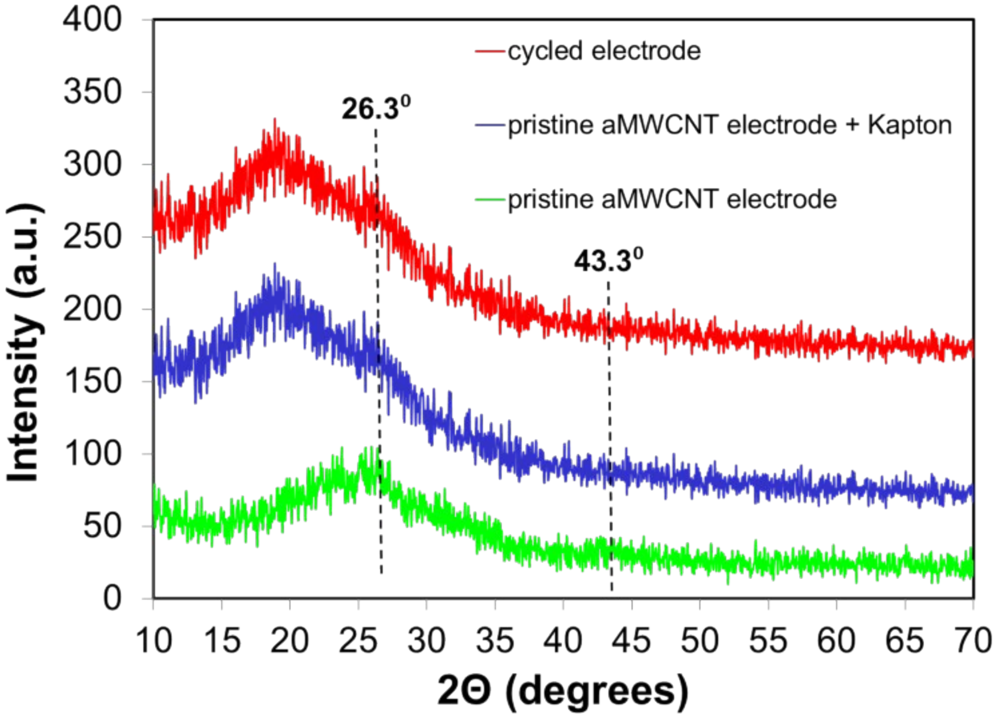


Figure S6: X-ray diffraction analyses of the as-prepared, pristine MWCNT electrode (green); the pristine electrode enclosed in Kapton film (blue) and the discharged MWCNT electrode sealed in Kapton (red). Peaks characteristic of graphitic MWCNT are seen at 26.3^0 and 43.3^0 in both the pristine and discharged electrodes.capture of dissolved polysulfides during charge and discharge.

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