Electronic Supplementary Information (ESI)

Simple Cathode Design for Li-S Batteries: Cell Performance and Mechanistic Insights by In Operando X-ray Diffraction

Jörn Kulisch,\textsuperscript{ab} Heino Sommer,\textsuperscript{ab} Torsten Brezesinski\textsuperscript{*a} and Jürgen Janek\textsuperscript{*ac}

\textsuperscript{a} Battery and Electrochemistry Laboratory, Institute of Nanotechnology, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany. E-mail: torsten.brezesinski@kit.edu, juergen.janek@kit.edu.

\textsuperscript{b} BASF SE, 67056 Ludwigshafen, Germany.

\textsuperscript{c} Institute of Physical Chemistry, Justus-Liebig-University Giessen, Heinrich-Buff-Ring 58, 35392 Giessen, Germany.
**Fig. S1** Morphology of non-calendered, $\sim$45 $\mu$m-thick sulfur cathodes on primed aluminum before galvanostatic cycling. (a) Low-magnification top view SEM image. (b) High-magnification cross-sectional SEM image.

**Fig. S2** Discharge profiles of the Li/S cells cycled at different temperatures. (a) 1st cycle performed at C/50. (b) 2nd cycle performed at C/5. As expected, the second plateau is shifted towards higher potential with increasing temperature due to faster reaction kinetics. The
significant differences in the first plateau on the 1st cycle might be related to the higher solubility and mobility of the higher-order lithium polysulfides in the electrolyte at elevated temperatures.

Fig. S3 (a, c) Specific charge (black triangles) and discharge (red circles) capacities versus cycle number. Regardless of whether the first 2 cycles or the 1st and 12th cycles are performed at a rate of C/50, the capacity loss is virtually the same. This result implies that the drop-off in
specific capacity levels off very quickly because the major active material loss occurs during the formation cycle at C/50. (b) Voltage profiles of the first 3 cycles, corresponding to (a).