

## Supporting Information

### Towards reliable three-electrode cells for lithium–sulfur batteries

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## 1. Experimental Information

The fabrication of the S/C composite electrodes follows a previously reported recipe,<sup>29</sup> consisting of 65% sulfur (S, Sigma-Aldrich), 21% Ketjenblack (KB, EC-600JD, Akzo Nobel), 3.5% Super C65 (Imerys), 3.5% carbon nanofibers (20–200 nm × 100 μm, Sigma-Aldrich), 5.6% poly(ethylene oxide) (Mw ~4 000 000, Sigma-Aldrich), 1.4% poly-(vinylpyrrolidone) (Mw ~360 000, Sigma-Aldrich) by weight. S and KB are first mixed in a mortar and heated to 155 °C for 20 min, then mixed with the rest of the components, isopropanol and deionised water (1:6:5, w:w) in a planetary ball mill for 2 h to form a slurry. The slurry is tape cast onto C-coated Al foil (20 μm thick, Showa Denko), dried in atmosphere and cut into ø13 mm discs, and then further dried at 5 mbar, 55 °C for 12 hr. For the three-electrode coin cells, the S/C composite and a ø17 mm Celgard®2024 separator are laid down first in the bottom part of an R2025 coin cell (Hohsen). A polyimide-wrapped Au microwire (ø50 μm, GoodFellow) is placed on the separator, followed by another separator, ø15 mm Li (125 μm thick, Cyprus Foote Mineral), a spacer and a washer spring. The Au microwire is fit to the groove of the gasket of the coin cell with a tweezer outside the glovebox beforehand to facilitate this process and decrease the chances of breaking the wire when closing the coin cell with the crimper. The amount of electrolyte according to the designated E/S ratio is added by a micropipette onto the separator in the gap between the space and gasket right before closing the cell with its cap. The electrolyte contains 1 m Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, BASF) and 0.25 m lithium nitrate (LiNO<sub>3</sub>, Sigma-Aldrich), which are dried at 120 °C under vacuum for 12 h, before mixing with the solvents: 1,2-Dimethoxyethane (DME, BASF) and 1,3-dioxolane (DOL, Sigma-Aldrich), which are dried with 3-Å molecular sieves. For the cells with LiAu RE, the Au microwire is lithiated by applying a constant current of 200 nA until its potential reaches 0.32 V against that of the metallic Li electrode and subsequently holding at the potential for 1 h. The cells in other cell formats in the ESI are made with the same components unless specified otherwise in the following. The two-electrode coin cells are made without the polyimide-wrapped Au microwire and with the E/S ratio and number of separators as specified. The pouch cell was made with one separator and E/S = 10. The customised cell (3e-Hohsen E/S = 10) is HS-3E model purchased from Hohsen Corp., which contains two ø24 mm Celgard®2024 separators and a ring (inner and outer radii: 18 and 22 mm, respectively) of metallic Li RE between the separators. The two- and three-electrode cells are tested using an Arbin BT-2043 battery testing system and Bio-Logic MPG 200 battery cycler, respectively, except for the first 8 cycles of the cell '3-e E/S = 7 LiAu', which is initially cycled on the former but switched to the latter after the 9<sup>th</sup> cycle. All the cells are galvanostatically cycled with the same protocol of the ICI method, which introduces a one-second current pause every five minutes,

and controlled by the cell voltage (measured on WE against CE). The cells are discharged at C/50 to 1.9 V and charged at C/25 to 2.6 V in the first cycle. Afterwards, the cells are cycled at C/10 between 1.8 and 2.6 V. The internal resistance (R) and diffusion resistance coefficient (k) are acquired by the ICI analysis<sup>15,25,26</sup> carried out with the R-programming language. The script and raw data can be found via zenodo, <https://doi.org/10.5281/zenodo.5211151>.

Please refer to the main text for the references in the experimental information.

## 2. Photograph of the three-electrode cell setup



Fig. S1 Photograph of the cell '3-e E/S=7 LiAu' as an example of the three-electrode cell setup. The polyimide-wrapped Au microwire can be observed on the left. Polyimide coating on the last 5 mm of the outer end of the wire was scraped off, and then clamped by a pair of a pin and a socket of the D-miniature electrical connector, which is held by the white crocodile clip.

### 3. Comparison between the electrochemical properties of the three- and two-electrode cells

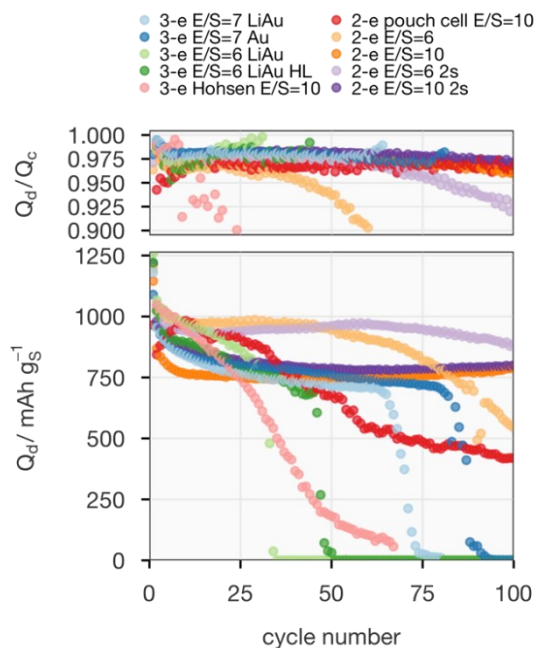


Fig. S2 Charge efficiency ( $Q_d/Q_c$ ) and specific discharge capacity ( $Q_d$ ) of all the cells up to the 100<sup>th</sup> cycle. Two-electrode coin cells with 2 separators are marked with '2s'. The sulfur-loading of the cell marked with 'HL' is 3.2  $\text{mg}_s \text{cm}^{-2}$  while that of the other cells is 2.0—2.5  $\text{mg}_s \text{cm}^{-2}$ .

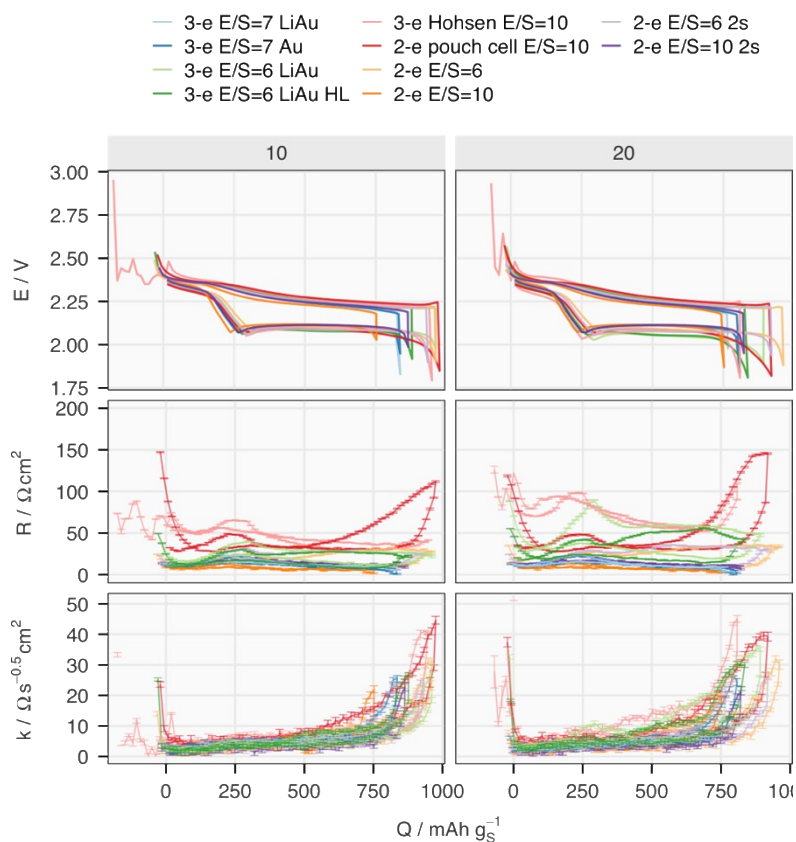


Fig. S3 Cell voltage ( $E$ ), internal resistance ( $R$ ) and diffusion resistance coefficient ( $k$ ) of the cell (WE against CE) of all the cells in the 10<sup>th</sup> and 20<sup>th</sup> cycle.

#### 4. Experimental parameters of the cells in this manuscript

Table S1. Experimental parameters of the cells in this manuscript. The electrodes are all made with the same coating recipe described in the experimental section in the “Notes and references” section of the manuscript. The electrode area is 1.327 cm<sup>2</sup> and the sulfur content is 65 wt%.

Cell label	Electrode mass / mg	Sulfur mass / mg	Electrolyte volume / $\mu\text{L}$	Sulfur-loading / $\text{mg cm}^{-2}$	E/S ratio / $\mu\text{L mg}^{-1}$
3-e E/S=7 Au	4.87	3.17	21.3	2.38	6.73
3-e E/S=7 LiAu	5.52	3.59	23.83	2.70	6.64
3-e E/S=6 LiAu	5.31	3.46	20.7	2.60	6.00
3-e E/S=6 LiAu HL	6.44	4.19	25.2	3.15	6.02
2-e E/S=10	5.17	3.36	33.6	2.53	10.0
2-e E/S=10 2s	5.21	3.39	33.87	2.55	10.0
2-e E/S=6	5.25	3.41	20.48	2.57	6.00
2-e E/S=6 2s	5.94	3.86	23.17	2.91	6.00
2-e pouch cell E/S=10	5.34	3.47	34.7	2.62	10.0
3-e Hohsen E/S=10	4.86	3.16	31.6	2.38	10.0

5. Potential and resistance profiles in the later cycles of the cells not included in Fig. 3

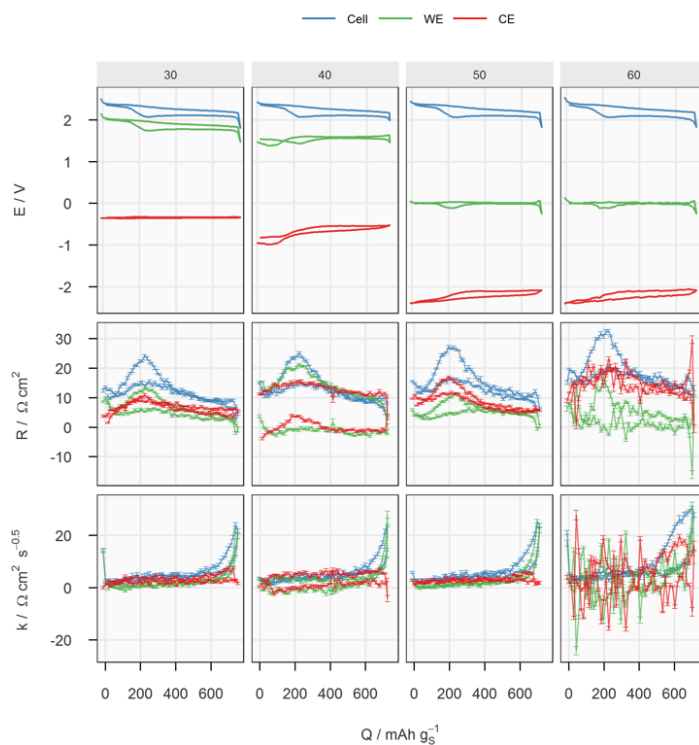


Fig. S4 Potential (E), internal resistance (R) and diffusion resistance coefficient (k) of the cell, working (WE) and counter (CE) electrodes in the 30<sup>th</sup>, 40<sup>th</sup>, 50<sup>th</sup> and 60<sup>th</sup> cycle of the cell with E/S = 7 and a LiAu RE, i.e. '3-e E/S=7 LiAu' in Fig. 2.

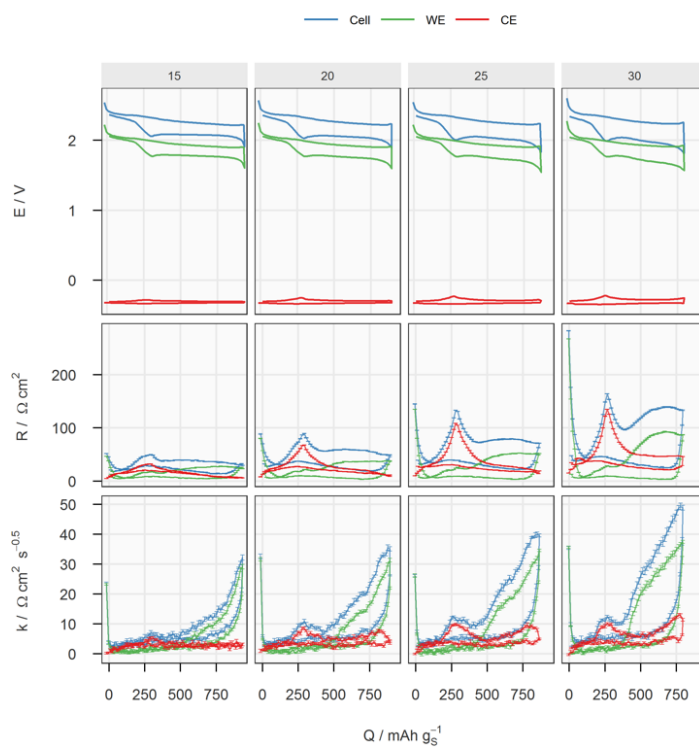


Fig. S5 Potential (E), internal resistance (R) and diffusion resistance coefficient (k) of the cell, working (WE) and counter (CE) electrodes in the 15<sup>th</sup>, 20<sup>th</sup>, 25<sup>th</sup> and 30<sup>th</sup> cycle of the cell with E/S = 6 and a LiAu RE, i.e. '3-e E/S=6 LiAu' in Fig. 2.

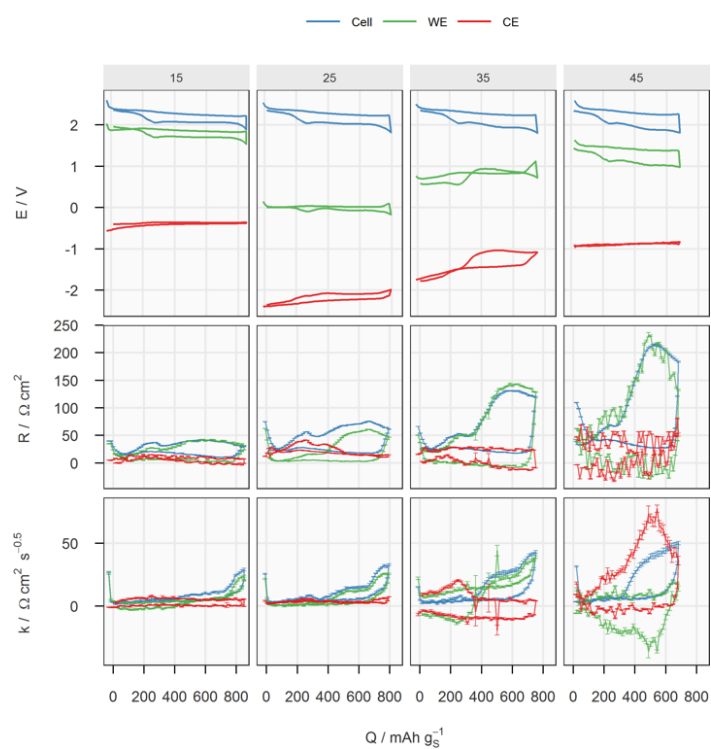


Fig. S6 Potential (E), internal resistance (R) and diffusion resistance coefficient (k) of the cell, working (WE) and counter (CE) electrodes in the 15<sup>th</sup>, 20<sup>th</sup>, 25<sup>th</sup> and 30<sup>th</sup> cycle of the cell with E/S = 6, high sulfur-loading and a LiAu RE, i.e. '3-e E/S=6 LiAu HL' in Fig. 2.



## 6. Statistics of the diffusion resistance coefficient (k)

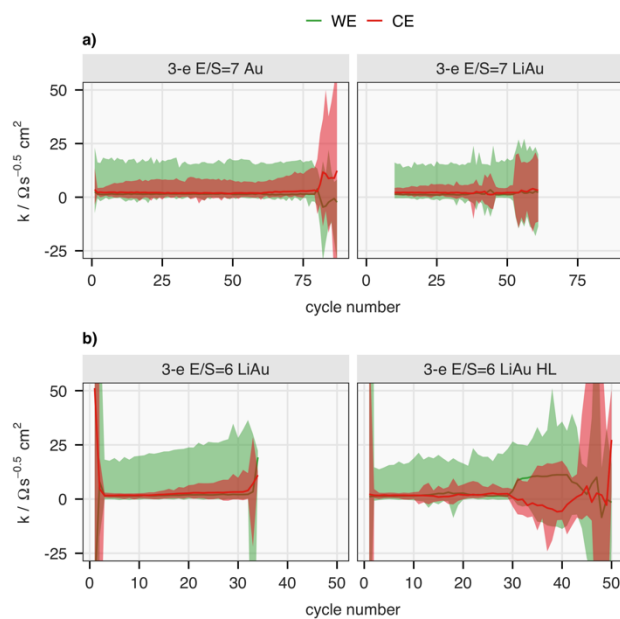


Fig. S7 The median (solid line), maximum and minimum (ribbon) of the diffusion resistance coefficient ( $k$ ) in each cycle of cells with a)  $E/S = 7$  and b)  $E/S = 6$ . Note that the scales are different in parts a and b. The maximum of the y-axis is set to  $50 \Omega s^{-0.5} \text{ cm}^2$  for the clarity. The data from first 9 cycles of the cell '3-e E/S=7 LiAu' have large noise in  $k$  due to the insufficient resolution of the potentiostat, which was changed after the 10<sup>th</sup> cycle.

## 7. Cycling statistics of all the coin cells

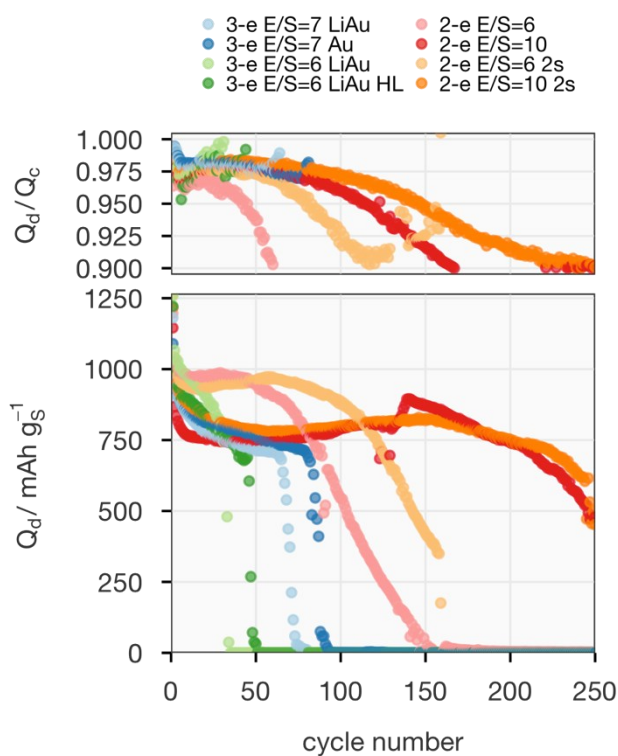


Fig. S8 Charge efficiency ( $Q_d/Q_c$ ) and specific discharge capacity ( $Q_d$ ) of all the coin cells. Two-electrode coin cells with 2 separators are marked with '2s'. The sulfur-loading of the cell marked with 'HL' is  $3.2 \text{ mg}_S \text{ cm}^{-2}$  while that of the other cells is  $2.0\text{--}2.5 \text{ mg}_S \text{ cm}^{-2}$ .