Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels. This journal is © The Royal Society of Chemistry 2020

## Investigating high-performance sulfur-metal nanocomposites for lithium batteries

Vittorio Marangon<sup>1,†</sup>, Daniele Di Lecce<sup>2,†</sup>, Fabio Orsatti<sup>1</sup>, Dan J.L. Brett<sup>2</sup>, Paul R. Shearing <sup>2,\*</sup>,

Jusef Hassoun<sup>1,3,\*</sup>

<sup>1</sup> University of Ferrara, Department of Chemical and Pharmaceutical Sciences, Via Fossato di

Mortara 17, 44121, Ferrara, Italy.

<sup>2</sup> Electrochemical Innovation Lab, Department of Chemical Engineering, UCL, London, WC1E

7JE, United Kingdom

<sup>3</sup> National Interuniversity Consortium of Materials Science and Technology (INSTM) University of

Ferrara Research Unit, University of Ferrara, Via Fossato di Mortara, 17, 44121, Ferrara, Italy.

Corresponding Authors: jusef.hassoun@unife.it, p.shearing@ucl.ac.uk.

† Authors equally contributed

**Electronic Supplementary Information** 

The electrode slurries were cast on a carbon-cloth foil (ELAT 1400, MTI Corp.), which has been elsewhere thoroughly characterized in terms of morphology, surface area, porosity, and surface chemistry.<sup>1</sup> Figure S1 (panels (a and b)) shows SEM images at two different magnifications of the carbon-cloth, revealing submicrometric carbon primary particles and a rough surface with micrometric cracks suitable for hosting the electrode material.



**Figure S1**. SEM images at two different magnifications of a pristine carbon-cloth electrode support. See the experimental section of the manuscript for further information.

Figure S2 shows a comparison of the X-ray diffraction (XRD) patterns of S:Sn 85:15 w/w (panel a) and S:Ni 85:15 w/w (panel b) with the sulfur and metal precursors. XRD confirms physical mixing of the components, thus indicating absence of undesired products formed by chemical reaction, except for negligible traces of SnO<sub>2</sub> due to minor oxidation of Sn under air (reflections at 29.86° and 33.3°

in panel a). The patterns reveal crystalline orthorhombic sulfur ( $\alpha$ -S<sub>8</sub>, ICSD # 27840), tetragonal tin (ICSD # 40038), and cubic nickel (ICSD # 672759) according to the reference data sheets.



**Figure S2**. XRD patterns of the S:Sn 85:15 w/w and S:Ni 85:15 w/w powders as well as the related components: (a) S:Sn 85:15 w/w composite (blue), tin (light blue) and sulfur (yellow); (b) S:Ni 85:15 w/w composite (green), nickel (light green) and sulfur (yellow). Reference data for elemental sulfur (yellow bars, ICSD # 27840), metallic tin (blue bars, ICSD # 40038) and metallic nickel (green bars, ICSD # 672759).

Figure S3 reports a volume rendering of reconstructed tomographic datasets of S:Sn 85:15 w/w (panel a) and S:Ni 85:15 w/w (panel b) aggregates. Imaging has been performed by a grayscale representation reflecting the actual attenuation of the X-ray beam within the sample, which is related to the material density. Thus, highly attenuating metallic clusters and lowly attenuating sulfur are unambiguously observed as bight and dark gray domains, respectively. X-ray computed tomography (CT) clearly shows the different arrangements of the two sulfur-metal aggregates. Indeed, Sn is intimately mixed with sulfur (panel a), while Ni mostly lays on the particle surface (panel b). Figure 1 in the manuscript reports further results and discussion on the characterization of S:Sn 85:15 w/w and S:Ni 85:15 w/w by various techniques.



**Figure S3**. Volume rendering using grayscale representation reflecting the X-ray attenuation of (**a**) S:Sn 85:15 w/w and (**b**) S:Ni 85:15 w/w particles as determined by X-ray nano-CT. Voxel size:  $63 \times 63 \times 63 \times 63$  nm<sup>3</sup>; microfocus rotating anode X-ray source set at 35 kV and 25 mA. Scans performed in X-ray absorption-contrast and large-field-of-view (65 µm) modes, by taking 1601 projections through 180° with exposure time of 46 and 55 s for S:Sn 85:15 w/w and S:Ni 85:15 w/w, respectively, and 1 voxel binning. See the related three-phase segmentation in Figure 1h-j and 1-n in the results and discussion section of the manuscript.

A diffusion-limited model based on the reports of Randles<sup>2</sup> and Sevcik<sup>3</sup> may empirically describe the electrochemical conversion processes occurring in the S:Sn 85:15 w/w and S:Ni 85:15 w/w electrodes according to the results of cyclic voltammetry measurements at several rates (panels e and f of Figure 2). Indeed, Figure S4 reveals a linear relation between the peak current ( $I_p$ ) and the square root of the scan rate ( $v^{l/2}$ ) in full agreement with the model, where panels a and b are referred to S:Sn 85:15 w/w and S:Ni 85:15 w/w, respectively, in spite of a small deviation of the intercept of the regression line from 0 A (see Table S1) which may be reasonably attributed to experimental errors and the approximations of the model. The slope obtained by linear regression has been used to calculate an apparent Li<sup>+</sup> diffusion coefficient (*D*) according to equation 1 (see the experimental section of the manuscript). Table S1 and bottom panels of Figure 2e, f report the related data.



**Figure S4**. Peak current ( $I_p$ ) *versus* the square root of the scan rate ( $v^{t/2}$ ) for the voltammograms of Figure 2e-f (top panels; see the results and discussion section of the manuscript) with related linear fits. CV measurements were performed at various scan rates (0.05, 0.1, 0.15, 0.2 and 0.25 mV s<sup>-1</sup>) on Li | DOL:DME 1:1 w/w, 1 mol kg<sup>-1</sup> LiTFSI, 1 mol kg<sup>-1</sup> LiNO<sub>3</sub> | cathode cells using the (**a**) S:Sn 85:15 w/w and (**b**) S:Ni 85:15 w/w electrodes within the potential range from 1.8 to 2.8 V *vs* Li<sup>+</sup>/Li. The following voltammetric peaks were considered: at 2.4 V *vs* Li<sup>+</sup>/Li during charge (2 electrons), 2.3 V *vs* Li<sup>+</sup>/Li during discharge (1 electron), and 2.0 V *vs* Li<sup>+</sup>/Li during discharge (1 electron). The Li<sup>+</sup> diffusion coefficients (*D*, Table S1) was calculated according to the Randless-Sevcik equation (see the experimental section and Figure 2e-f in the results and discussion section of the manuscript for further details). Measurements performed at 25 °C.

Material	State of charge	Intercept (A)	Slope $(A s^{1/2} V^{-1/2})$	$D \\ (cm^2 s^{-1})$
S:Sn 85:15 w/w	2.3 V vs Li <sup>+</sup> /Li (disch.)	(4.2±0.3)×10 <sup>-4</sup>	$-0.209 \pm 0.003$	$6.4 \times 10^{-8}$
	2.0 V vs Li <sup>+</sup> /Li (disch.)	(-1.93±0.12)×10 <sup>-3</sup>	-0.366±0.010	4.9×10 <sup>-8</sup>
	2.4 V vs Li <sup>+</sup> /Li (ch.)	(1.1±0.2)×10 <sup>-3</sup>	$0.42 \pm 0.02$	3.2×10 <sup>-8</sup>
S:Ni 85:15 w/w	2.3 V vs Li <sup>+</sup> /Li (disch.)	(4.5±0.7)×10 <sup>-4</sup>	-0.272±0.006	1.1×10 <sup>-7</sup>
	2.0 V vs Li <sup>+</sup> /Li (disch.)	(-2.3±0.2)×10 <sup>-3</sup>	$-0.452\pm0.014$	$7.5 \times 10^{-8}$
	2.4 V vs Li <sup>+</sup> /Li (ch.)	(2.6±0.4)×10 <sup>-3</sup>	0.41±0.03	3.0×10 <sup>-8</sup>

**Table S1**. Li<sup>+</sup> diffusion coefficient (*D*) values at various states of charge for Li | DOL:DME 1:1 w/w, 1 mol kg<sup>-1</sup> LiTFSI, 1 mol kg<sup>-1</sup> LiNO<sub>3</sub> | cathode cells using the S:Sn 85:15 w/w and S:Ni 85:15 w/w electrodes. *D* was determined through CV measurements at various scan rates (0.05, 0.1, 0.15, 0.2 and 0.25 mV s<sup>-1</sup>; potential range:  $1.8 - 2.8 \text{ V } vs \text{ Li}^+/\text{Li}$ ) by applying the Randless-Sevcik equation (see the experimental section and Figure 2e-f in the results and discussion section of the manuscript, as well as Figure S4, for further information). Intercept and slope of the related linear fit are also shown. Measurement performed at 25 °C.

A thorough *ex situ* analysis of the nanocomposite S:Sn 85:15 w/w and S:Ni 85:15 w/w electrodes has been carried out by means of XRD, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and X-ray micro-CT. Electrodes were galvanostatically cycled in lithium coincells at a C/3 rate (1C = 1675 mA  $g_s^{-1}$ , Figure S5) and analyzed after cell disassembly at the end of the 1<sup>st</sup> and the 10<sup>th</sup> cycles. Pristine electrode samples were also analyzed (see the experimental section of the manuscript for further details about cycling, cell disassembly, and *ex situ* analysis).



**Figure S5**. Voltage profiles of the first and tenth galvanostatic cycles at a C/3 rate ( $1C = 1675 \text{ mA gs}^{-1}$ ) of Li | DOL:DME 1:1 w/w, 1 mol kg<sup>-1</sup> LiTFSI, 0.4 mol kg<sup>-1</sup> LiNO<sub>3</sub> | cathode cells employing (**a**) S:Sn 85:15 w/w and (**b**) S:Ni 85:15 w/w electrodes within the voltage range from 1.9 to 2.8 V. Measurements performed at 25 °C. The cells were subsequently disassembled in an Ar-filled glovebox (O<sub>2</sub> and H<sub>2</sub>O content below 1 ppm) in order to recover the cathodes. The electrodes were dried for 30 min under vacuum and studied by XRD (both after 1 and 10 cycles; Figure 3a-b in the results and discussion section of the manuscript), SEM-EDX (both after 1 and 10 cycles; Figure S6 in the Supplementary Information), and X-ray micro-CT (after 1 cycle; Figure 3c-j, Figure 4, and Figure S7 in the results and discussion section of the manuscript and hereafter in Electronic Supplementary Information section, respectively; see the experimental section for further details).

Panels a and b of Figure S5 show the related voltage profiles indicating the states of charge of the *ex situ* measurements, while Figure S6 reports the related SEM-EDX imaging. The overall time required for a full cycle based on the theoretical capacity of sulfur should be 6 hours. However, the S:Sn 85:15 w/w and S:Ni 85:15 w/w electrodes deliver an actual capacity of about 1000 and 1390 mAh  $g_s^{-1}$  at the C/3 rate in our optimized cell configuration (see Figure 5), thereby leading to a maximum cycle time within 3.6 and 5.0 h. As mentioned in the experimental section, the cells for *ex situ* characterization were crimped with a moderately lower pressure than usual. Such a precaution remarkably facilitates the disassembling, but slightly decreases the capacity due to a moderately higher cell polarization, thereby leading to an overall cycle time within 3.4 and 4.1 h. The morphological analysis indicates substantial electrode changes after cycling, as discussed in detail in the manuscript (Figure 3 and 4 in the results and discussion section).

Panels a, e, i, and m of Figure S7 display cross-sectional slices extracted in a plane parallel to the electrode surface from three-dimensional reconstructions of the micro-CT datasets. The slices are represented according to a grayscale indicating the X-ray attenuation by the various phases as already discussed for Figure S3. X-ray micro-CT suggests a different morphology for S:Sn 85:15 w/w and S:Ni 85:15 w/w, as well as major microstructural reorganizations after the first cycle, as extensively examined in the manuscript (discussion of Figures 3 and 4). Panels b, f, j, and n of Figure S7 illustrate the grayscale thresholding segmentation based on X-ray attenuation, which allows a clear view of the various domains distributed over the slice. Related three-dimensional rendering for the sulfur-metal domains unequivocally shows the massive rearrangements after cycling (panels c, g, k, o). Sphericity distribution histograms have been calculated according to equation 2 in the experimental section of the manuscript by considering the sulfur phase and the sulfur-metal intimate mixture domains, respectively depicted in yellow, light blue and light green in Figures 3, 4, and S7. Further analysis and discussion on the micro-CT data is reported in the manuscript. Moreover, Movies S1, S2, S3, and S4 show animations of the three-dimensional reconstructions and all the cross-sectional slices orthogonal to the cathode surface.



**Figure S6**. SEM-EDX images of the (**a-f, m-r, y-di**) S:Sn 85:15 w/w and (**g-l, s-x, ei-ji**) S:Ni 85:15 w/w electrodes (**a-l**) in the pristine state, (**m-x**) after 1 cycle, and (**y-ji**) after 10 cycles. In detail: (**a, g, m, s, y, ei, f, l, r, x, di, ji**) SEM images at different magnifications; (**b-e, h-k, n-q, t-w, z-ci, fi-ii**) EDX maps of S, Sn, Ni, C, F, and O over the electrode. Galvanostatic cycling was performed at a C/3 rate ( $1C = 1675 \text{ mA } g_s^{-1}$ ) and 25 °C on Li | DOL:DME 1:1 w/w, 1 mol kg<sup>-1</sup> LiTFSI, 0.4 mol kg<sup>-1</sup> LiNO<sub>3</sub> | cathode cells employing S:Sn 85:15 w/w and S:Ni 85:15 w/w electrodes within the voltage range from 1.9 to 2.8 V. The cells were disassembled in an Ar-filled glovebox (O<sub>2</sub> and H<sub>2</sub>O content below 1 ppm) in order to recover the cathodes. The electrodes were dried for 30 min under vacuum before further investigations. See the related voltage profiles in Figure S5 as well as the XRD and X-ray micro-CT analyses in Figures 3, 4 and S7 in the results and discussion section of the manuscript and in the Electronic Supplementary Information, respectively.



**Figure S7.** X-ray micro-CT analysis of (**a-d, i-l**) S:Sn 85:15 w/w and (**e-h, m-p**) S:Ni 85:15 w/w electrode samples (**a-h**) before and (**i-p**) after 1 discharge/charge cycle at a constant current rate of C/3 (1C = 1675 mA  $gs^{-1}$ ) in Li | DOL:DME 1:1 w/w, 1 mol  $kg^{-1}$  LiTFSI, 0.4 mol  $kg^{-1}$  LiNO<sub>3</sub> | cathode cells (voltage range: 1.9 – 2.8 V). In detail: (**a, e, i, m**) slice extracted in a plane parallel to the electrode surface with (**b, f, j, n**) corresponding segmentation (S: yellow; Sn: blue; S-Sn intimate mixture: light blue; Ni: green; S-Ni intimate mixture: light green; carbon/binder/carbon-cloth: gray; exterior: black); (**c, g, k, o**) segmented volume rendering (S: yellow; Sn: blue; S-Sn intimate mixture: light blue; Ni: green; S-Ni intimate mixture: light green); (**d, h, l, p**) sphericity (shape factor) distribution of the S and S-metal domains (see the related particle size distribution analysis of the micro-CT datasets in panels b, d, f, and h of Figure 4 in the results and discussion section of the manuscript). Voxel size: from 288×288×288 to 373×373×373 nm<sup>3</sup>; field of view: from about 570 to about 730 µm. X-ray source set at 80 kV and 88 µA. Scan performed by using a 20X objective lens and taking 1601 projections through 360° with an exposure time from 22 to 40 s and 1 voxel binning (see the experimental section for further details, Figures 3 and 4 in the results and discussion section and cross sectional slices).

Several casting tests of S:Sn 85:15 w/w and S:Ni 85:15 w/w on Cu foils (see the experimental section of the manuscript for further details of the casting procedure) suggest possible corrosion of the current collector by reaction with sulfur. Figure S8a shows the XRD patterns of the Cu-current collectors after the casting process and photographic images of the pristine (left-hand side disk) and corroded (right-hand side disk) Cu foils in inset. XRD reveals Cu<sub>2</sub>S after casting and a dark-grey to black rough layer is observed over the current collector. Such a massive corrosion leads to the full electrode deactivation, as shown in Figure S8b and c.

Figure S9a-b illustrates the rate performances of the S:Sn 85:15 w/w (a) and S:Ni 85:15 w/w (b) electrodes in terms of voltage profiles. The data, broadly discussed in the manuscript (Figure 6a and b), reveal remarkable rate capability despite the expected increase of cell polarization by raising the current, as well as promising energy and power performances. Figure S9c-d shows the voltage profile of galvanostatic tests at a 1C rate ( $1C = 1675 \text{ mA gs}^{-1}$ ) of lithium cells using the (c) S:Sn 85:15 w/w and (d) S:Ni 85:15 w/w composites in combination with a diglyme-based electrolyte, *i.e.*, diethylene glycol dimethyl ether (DEGDME) dissolving LiTFSI and LiNO<sub>3</sub> in a concentration of 1 mol kg<sup>-1</sup> with respect to the solvent mass. The cells show a rather stable response upon 300 cycles with a promising capacity retention and a relatively low polarization.



**Figure S8**. (a) XRD of copper current collector after doctor-blade casting of S:Ni 85:15 w/w (Cu 1, green) and S:Sn 85:15 w/w (Cu 2, blue) and electrode drying with indication of Cu (<sup>+</sup> symbol, PDF # 85-1326) and Cu<sub>2</sub>S (\* symbol, PDF # 84-0209) peaks. Insets: photographic images of Cu 1 (green) and Cu 2 (blue) before (left-hand side disks) and after (right-hand side disks) doctor-blade casting and electrode drying. (**b-c**) 1<sup>st</sup> and 2<sup>nd</sup> cycle voltage profiles of galvanostatic measurements at a C/3 rate performed on Li | DOL:DME 1:1 w/w, 1 mol kg<sup>-1</sup> LiTFSI, 1 mol kg<sup>-1</sup> LiNO<sub>3</sub> | cathode cells employing the (**b**) S:Sn 85:15 w/w and (**c**) S:Ni 85:15 w/w composites cast on Cu current collector (1C = 1675 mA gs<sup>-1</sup>). Voltage range: 1.9 – 2.8 V Specific capacity as referred to the sulfur mass. Measurements performed at 25 °C.



**Figure S9**. (**a-b**) Voltage profiles of the rate capability tests reported in Figure 6 of the manuscript (results and discussion section). Tests performed on Li | DOL:DME 1:1 w/w, 1 mol kg<sup>-1</sup> LiTFSI, 1 mol kg<sup>-1</sup> LiNO<sub>3</sub> | cathode cells using the (**a**) S:Sn 85:15 w/w and (**b**) S:Ni 85:15 w/w composites at C/10, C/8, C/5, C/3, C/2, 1C, 2C, 3C, 4C, 5C, 8C and 10C rates (1C = 1675 mA gs<sup>-1</sup>). Voltage range: 1.9 - 2.8 V *vs* Li<sup>+</sup>/Li from C/10 to C/2 and 1.8 - 2.8 V from 1C to 10C. (**c-d**) Voltage profiles of galvanostatic measurements performed on Li | DEGDME, 1 mol kg<sup>-1</sup> LiTFSI, 1 mol kg<sup>-1</sup> LiNO<sub>3</sub> | cathode cells employing the (**c**) S:Sn 85:15 w/w and (**d**) S:Ni 85:15 w/w composites. Tests performed at a 1C rate (1C = 1675 mA gs<sup>-1</sup>) within the voltage range of 1.8 - 2.8 V. See Figure 6e in the results and discussion section of the manuscript for the corresponding cycling trends with coulombic efficiency. Specific capacity as referred to the sulfur mass. Measurements performed at 25 °C.