

Dimensional analysis and intercomparison of the basin time of concentration formulas

*Original*

Dimensional analysis and intercomparison of the basin time of concentration formulas / Evangelista, Giulia; Claps, Pierluigi. - ELETTRONICO. - (2022). (Intervento presentato al convegno EGU General Assembly 2022 tenutosi a Vienna, Austria nel 23 - 27 Maggio 2022) [10.5194/egusphere-egu22-471].

*Availability:*

This version is available at: 11583/2964811 since: 2022-05-29T10:24:34Z

*Publisher:*

Copernicus GmbH

*Published*

DOI:10.5194/egusphere-egu22-471

*Terms of use:*

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

*Publisher copyright*

AIP postprint versione editoriale con licenza CC BY/Version of Record with CC BY license

Copyright 2022 Author(s). This article is distributed under a Creative Commons Attribution (CC BY) License <https://creativecommons.org/licenses/by/4.0/>."

(Article begins on next page)

# Molybdenum disulfide/polyaniline interlayer for lithium polysulphide trapping in lithium-sulfur batteries

*Daniele Versaci<sup>a\*</sup>, Irene Canale<sup>a</sup>, Sumita Goswami<sup>b</sup>, Julia Amici<sup>a</sup>, Carlotta Francia<sup>a</sup>, Elvira Fortunato<sup>b</sup>, Rodrigo Martins<sup>b</sup>, Luís Pereira<sup>b,c</sup>, Silvia Bodoardo<sup>a</sup>.*

<sup>a</sup> Electrochemistry Group, Department of Applied Science and Technology (DISAT), Politecnico di Torino, C.so Duca degli Abruzzi 24, 10129 Torino (Italy)

<sup>b</sup> CENIMAT/i3N Department of Materials Science NOVA School of Science and Technology NOVA University Lisbon (FCT-NOVA) and CEMOP/UNINOVA Campus de Caparica, Caparica 2829-516, Portugal

<sup>c</sup> ALMASCIENCE Colab, Campus da Caparica, 2829-516 Caparica, Portugal

\*Corresponding authors:

Daniele Versaci, Tel.: +39 011 090 4789; E-mail address: [daniele.versaci@polito.it](mailto:daniele.versaci@polito.it);

**KEYWORDS:** Lithium-sulfur battery, polyaniline, molybdenum sulphide, cathode, interlayer

## 19    **ABSTRACT**

20        Lithium-sulphur battery technology promises much higher energy storage capacity compared to  
21        common Li-ion commercial batteries. Li-S batteries have high theoretical capacity of 1672 mAh g<sup>-1</sup>,  
22        thanks to conversion reaction from solid sulphur to lithium polysulfides (LiPSs). Unfortunately, few  
23        issues are still hindering their commercialization. The main problem afflicting lithium sulphur  
24        batteries is the shuttle phenomenon, due to soluble long chain LiPSs generated at the cathode. In the  
25        last years, many interlayer separators have been based on materials showing physical blocking of  
26        LiPSs. In particular, MoS<sub>2</sub> and PANI separately showed strong adsorption capability, preventing  
27        polysulfides dissolution and accelerating the redox reaction kinetics. In the present work we  
28        rationally design, for the first time, composite materials based on PANI and MoS<sub>2</sub>, with the aim to  
29        evaluate the specific role of each component and their synergy as LiPSs blocking-agents, by  
30        implementation of a second layer containing the MoS<sub>2</sub>/PANI composite directly on the top of the  
31        standard S/C electrode. The systematic study confirms that double-layer containing the composite  
32        remarkably improves the performance of the sulphur cathode, showing specific capacity close to  
33        600 mAh g<sup>-1</sup>, which is 42 % higher than the standard sulphur cathode, after 500 cycles.

34

## 1. INTRODUCTION

Lithium-sulphur (Li-S) battery technology promises much higher energy storage capacity compared to common Li-ion commercial batteries. Sulphur undergoes through a conversion reaction and forms lithium polysulfides (LiPSs) [1], allowing larger accommodation of ions and electrons (two per sulphur atom) [2], conferring sulphur batteries an incredibly high theoretical capacity of 1672 mAh g<sup>-1</sup> [3][4][5]. At the same time, sulphur grants a wide range of operation temperature, being a non-toxic abundant and low-cost element [6][7].

The reaction occurring in the lithium-sulphur battery is a conversion reaction involving a multi-step process. More in detail, during discharge, lithium ions and electrons are generated at the anode and move to the cathode side [2][8]. The electrons reach the sulphur cathode where the S<sub>8</sub> ring is reduced, forming high order lithium polysulfides (LiPSs, Li<sub>2</sub>S<sub>x</sub> (4 > x ≤ 8)), which are soluble in the liquid electrolyte and responsible for 25 % of the discharge capacity. As the discharge proceeds, high order LiPSs get further reduced to low order LiPSs [7][9][10], which are responsible for the remaining 75 % of gravimetric capacity [11]. During charge the reverse reactions occur, converting low order LiPSs back to high order LiPSs and sulphur.

Despite many advantages, few issues are still hindering the commercialization of Li-S battery. The first problem is the poor electrode reaction kinetics, due to the insulating nature of sulphur and the low electronic and ionic conductivity of Li<sub>2</sub>S [12]. A second problem is the volume expansion occurring during charge and discharge processes, which decreases the contact between current collector and active material.

Nevertheless, the main issue of lithium sulphur batteries is the shuttle phenomenon, due to soluble long chain LiPSs [8], which are able to migrate to the anode where they directly react with lithium, by parasitic passivation reactions [12][13][14]. Typically, the shuttle phenomenon takes the

58 battery to an infinite recharge state resulting in poor coulombic efficiency [9]. Furthermore, high  
59 order LiPS slowly dissolve in the electrolyte, even in resting state, continuously decreasing the open  
60 circuit voltage and generating the self-discharge of the cell [1][10].

61 Conductive mesoporous carbons as material hosts for sulphur are useful to limit the shuttle  
62 phenomenon in lithium sulphur battery. However, carbon materials can only guarantee physical  
63 confinement of polysulfides [15][16], while chemical interactions between the non-polar carbon  
64 host and the polar  $\text{Li}_2\text{S}_x$  is inconspicuous [17][18][19].

65 In order to solve problems related to LiPSs shuttling and self-discharge, different approaches  
66 were proposed. One of the most interesting consists in a cathode overlayer, which is able to adsorb  
67 LiPSs and physically or chemically trap them. The implementation of a second layer directly coated  
68 on the sulphur cathode surface limits LiPSs shuttling and increase charge capacity, long term  
69 performances and battery lifetime.

70 Currently, most interlayers are based on materials showing great physical blocking of LiPSs, like  
71 graphene. Unfortunately, some are still not effective in preserving long cycle performances [20]. It  
72 was recently demonstrated that metal sulphides can directly interact with lithium polysulfides  
73 through electrostatic or chemical bonds, inhibiting the dissolution of LiPSs [18]. In particular,  
74 molybdenum disulphide ( $\text{MoS}_2$ ) showed strong adsorption capability, preventing polysulfides  
75 dissolution and accelerating the redox reaction kinetics of polysulfides conversion [21][22][23][24].

76 Two-dimensional  $\text{MoS}_2$  is widely used in electronic devices thanks to its physical and chemical  
77 properties, tuneable surface features, unique electronic structures, earth abundance and low cost.  
78  $\text{MoS}_2$  can interact with LiPSs by a strong polar metal–sulphur bonds or by a less strong dipolar  
79 interaction through the polarized surface [19][25]. Both these interactions can effectively inhibit  
80 polysulfides dissolution inside the electrolyte [14][18][26], increasing the performance of the

81 system. In addition, MoS<sub>2</sub> promotes the redox reaction kinetics of LiPSs (from long-chain to short-  
82 chain polysulfides) during the discharge/charge processes, acting as a lithium ion conductor. This  
83 way, the fast conversion of the soluble polysulfides decreases their accumulation into the electrolyte  
84 and inhibits their subsequent loss from the electrode [19][25][27]. In general, MoS<sub>2</sub> layers provide a  
85 large active conductive surface area ideal for a successful PS trapping, with great flexibility.  
86 However, both the absorption of the polysulphides and the catalytic activity strongly depend on  
87 chemical composition, surface functionality and intrinsic electronic structure of the catalyst  
88 [19][26][27]. Typically, the redox reactions occur through strong polysulfides adsorption, rapid  
89 interfacial charge transfer and product deposition. This means that the variation of surface  
90 adsorption behaviour can tune the activation energies of chemical reactions and promote the redox  
91 reaction kinetics [19]. These are at the basis of the higher electrochemical activity of MoS<sub>2</sub> with  
92 sulphur-free locations [28] and the stronger interaction between the edge sites of MoS<sub>2</sub> and LiPSs  
93 than those of basal surface sites [25]. Last but not least, the different phase structures of MoS<sub>2</sub>  
94 (hexagonal and tetragonal symmetry) have different catalytic behaviours as a consequence of  
95 different electronic properties [18][26][27].

96 At the same time, polar polymeric materials are often introduced into Li-S cells, in order to  
97 provide strong chemisorption anchoring sites for lithium polysulfides species [25]. It is well known  
98 that long chain polysulfides dissolution into the liquid electrolyte can be reduced through chemical  
99 interaction between Lewis acid-base interaction [16]. In this frame, polyaniline in the half-oxidized  
100 emeraldine base (EB) state was introduced in lithium-sulphur batteries thanks to its high thermal  
101 and environmental stability, mechanical flexibility, simple synthesis routes, but in particular to its  
102 ability to enhance conductivity and prevent the shuttle phenomenon [15][29]. Polyaniline has been  
103 largely used in Li-S batteries through different strategies, such as: coating layer [30], conductive  
104 host [31], covalent bond compounds [32], separator modifier/interlayer [33][34]. Moreover, PANI

105 was widely implemented as sulphur wrapping or grafting agent, in combination with other materials  
106 such as mesoporous carbons [35][36], graphene [37], multi walled carbon nanotubes [38][39] and  
107 others [40][41][42][43]. In all cases, PANI constitutes an excellent conductive matrix, providing  
108 conductive links between the sulphur and carbon particles. In fact, the crosslinked PANI network  
109 facilitates the ion permeation promoting a fast electron transfer, improving the mechanical  
110 properties of the electrodes and buffering the volume changes [15][34].

111 Nevertheless, one of the most important properties of positively charged PANI is its ability to  
112 adsorb negatively-charged lithium polysulfides, inhibiting/preventing their dissolution inside the  
113 electrolyte. In fact, the repetitive phenylenediamine and quinone diimine units give to polyaniline  
114 specific electrical conductivity and unique redox behaviour. In particular, the N-containing groups  
115 such as the quinonoid imine group ( $-NH^+=$  /  $-N=$ ) shows an electrocatalytic effect resulting as  
116 efficient redox mediator for long-chain lithium polysulfides conversion [15][32][34]. For these  
117 reasons PANI generally improves the electrochemical performance of sulphur cathodes, enhancing  
118 the cycling stability of the Li-S cell [15][34].

119 In summary, polyaniline and  $MoS_2$  are suitable materials able to anchor lithium polysulfides  
120 through both chemical and physical interactions. These materials can be easily deposited either on  
121 the separator or directly on the cathode, assuring ion transport thus helping to improve battery life  
122 cycle and efficiency [13][17].

123 Unlike previous reports, which separately investigate the role of PANI and  $MoS_2$ , in this work we  
124 study PANI/ $MoS_2$  composites, with the purpose of evaluating the different role of each component  
125 as LiPSs blocking agents. To date, a systematic study, properly comparing the role PANI/ $MoS_2$   
126 composites as LiPSs blocking agent and the different behavior of the two components is lacking. In  
127 addition, most published studies are difficult to compare, because of different test parameters, such  
128 as sulphur mass loading, electrolyte uptake, or different type of LiPSs blocking strategies (see Table

129 SI1). Therefore, we rationally design binary materials, which are implemented in a lithium sulphur  
130 cell using a double-layer approach, simply introducing a second layer directly on top of the standard  
131 S/C cathode.

132

## 133 **2. EXPERIMENTAL SECTION**

### 134 **2.1. Material preparation**

135 The composites were obtained simply mixing PANI and MoS<sub>2</sub> in an aqueous media. PANI and  
136 MoS<sub>2</sub> have been introduced with different ratios (0:100, 30:70, 70:30 and 100:0) to compare and  
137 better understand the influence and the role of each component on the final properties of the  
138 composites.

139 For PANI synthesis, a solution containing Aniline (0.2 M, Sigma Aldrich, purity  $\geq$  99.5 %)-and  
140 H<sub>2</sub>SO<sub>4</sub> (0.5 M, Sigma Aldrich, purity 95 – 97%) was prepared and then chemically treated with  
141 PSA ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 1 M, Sigma Aldrich, purity  $>$  98 %) which was added dropwise until the colour  
142 of the samples turned to dark green. The reaction was left on magnetic stirring overnight and the  
143 resulting precipitate was washed with distilled water and ethanol several times by centrifuge, until a  
144 neutral pH was reached. The dark green powder was collected and dried at 50 ° C overnight [45].  
145 This way, polyaniline powder was obtained separately and only in a second time was combined  
146 through sonication with commercial MoS<sub>2</sub> (hexagonal molybdenum (IV) sulfide, powder,  $<$  2 $\mu$ m,  
147 99%).

148 As few MoS<sub>2</sub> layers have significantly better properties than the bulk form, an exfoliation process  
149 was carried out on commercial bulk MoS<sub>2</sub>. Typically, the exfoliation of commercial MoS<sub>2</sub> requires  
150 a "solvent-assisted" process in which solvents with surface tension as close as possible to the  
151 surface energy of MoS<sub>2</sub> are adopted. In our case, MoS<sub>2</sub> powder was placed in a beaker containing



152 water and PANI and was subjected to ultra-sonication process for 9 hours at 300 W, avoiding the  
153 use of other solvents or additives. The selected ratio adopted between MoS<sub>2</sub> and PANI were: 100:0,  
154 0:100, 30:70 and 70:30 wt%, respectively named: MoS<sub>2</sub>, PANI, MoS<sub>2</sub>:PANI 3:7 and MoS<sub>2</sub>:PANI  
155 7:3. This choice was made in order to discriminate the contribution and the role of the two  
156 components on the final electrochemical performances.

157

## 158 **2.2. Material characterization**

159 XRD analysis was carried out by a PANalytical X'Pert (Cu Ka radiation) diffractometer. Data  
160 were collected with a 2D solid state detector (PIXcel) from 10 to 80° 2 $\theta$  with a step size of 0.026 2 $\theta$   
161 and a wavelength of 1.54187 Å.

162 Fourier Transform Infrared Spectroscopy (FTIR) was measured with a Nicolet™ iS50 FTIR  
163 spectrometer (Thermo Scientific™) equipped with ATR tool. 32 scans were collected with a  
164 resolution of 4 cm<sup>-1</sup> from 4000 to 400 cm<sup>-1</sup>.

165 FESEM analysis was carried out by Zeiss SUPRA™ 40 with Gemini column and Schottky field  
166 emission tip (tungsten at 1800 K). Acquisitions were made at acceleration voltage of 3 kV and  
167 working distance (WD) between 2.1 - 8.5 mm, with magnification up to 1000 KX.

168 Raman spectroscopy was performed in a Renishaw inVia Reflex micro-Raman spectrometer  
169 equipped with an air-cooled CCD detector and a HeNe laser, operating at 50 mW of 532 nm laser  
170 excitation. The laser beam was focused with a Leica objective lens (N Plan EPI), with a numerical  
171 aperture of 0.75. An integration time of 3 scans of 1.5 s each was used for all single-scan  
172 measurements. The intensity of the incident laser was 2.5 mW.

173 The UV-Vis absorption spectra were detected by a UV-vis spectrophotometer (JENWAY, 6850  
174 UV/Vis. Spectrophotometer) within the spectral range of 200 - 800 nm.

### 175 **2.3. Electrochemical measurements**

176 All working electrodes were prepared by solvent tape casting method. The so called “standard”  
177 sulphur cathode electrode (SL) was prepared using pure sulphur (Sigma Aldrich  $\geq 99.5\%$ ) as active  
178 material, Ketjenblack® (KjB, EC-300J, AkzoNobel), as conductive carbon additive and  
179 poly(vinylidenedifluoride) (PVdF, Kynar 761, Arkema; 10 wt.% in N-methyl-2-pyrrolidinone  
180 solution) as polymeric binder. The standard single-layer electrode composition was set up to  
181 70:30:10 wt%, respectively for S:KjB:PVdF, in all experiments. Ketjenblack® carbon was selected  
182 because is an inexpensive and highly conductive carbon, with high specific surface area and high  
183 pore volume, which are optimal properties to confine sulphur [46]. The S/KjB mixture (SL) was  
184 mechanically deposited on the aluminium current collector by an automatic film applicator (Sheen  
185 1133N) with a speed of  $50\text{ mm s}^{-1}$ , adjusting the Doctor Blade thickness at  $200\text{ }\mu\text{m}$ . The wet  
186 electrode was dried in an oven at  $50\text{ }^{\circ}\text{C}$  in air. A similar procedure was used to obtain double layer  
187 (DL) cathodes. The dried single-layer electrode was subsequently coated by a second layer  
188 containing  $\text{MoS}_2$ , PANI or a mixture of them. The ratio between  $\text{MoS}_2$  and/or PANI, KjB and  
189 PVDF, was 80:10:10, with a blade thickness of  $200\text{ }\mu\text{m}$ .

190 After solvent evaporation in air, disks of  $1.76\text{ cm}^2$  were punched out, vacuum dried at  $40\text{ }^{\circ}\text{C}$  (in a  
191 Büchi Glass Oven B-585) for 4 h, then transferred into an Argon filled dry glove-box (MBraum  
192 Labstar,  $\text{H}_2\text{O}$  and  $\text{O}_2$  content  $< 1\text{ ppm}$ ) for cell assembly. The active material loading of the  
193 “standard” sulphur cathode was  $\sim 1 - 1.2\text{ mg cm}^{-2}$ .

194 The electrochemical characterization was carried out in CR2032 coin cells, with lithium disk  
195 (Chemetall Foote Corporation,  $\varnothing 16\text{ mm}$ ) as counter electrode and PP polymeric membrane

196 (Celgard 2500, 25  $\mu\text{m}$  thickness,  $\varnothing$  19 mm) as separator. The electrolyte was a solution of 1,2-  
197 dimethoxyethane (DME) and 1,3-dioxolane (DIOX) 1:1 (v/v) with 1.0 M lithium  
198 bis(trifluoromethanesulfonyl)imide ( $\text{CF}_3\text{SO}_2\text{NLiSO}_2\text{CF}_3$ , LiTFSI) and 0.25 M lithium nitrate  
199 ( $\text{LiNO}_3$ ,  $\geq 99.9\%$  Sigma Aldrich). The solution was stored in argon filled glove box for at least 12  
200 h before the use. The electrolyte amount for each kind of experiment never exceeded 20  $\mu\text{L}$ ,  
201 corresponding to  $\sim 10 - 11 \mu\text{L mg}^{-1}$  (referred to S amount).

202 The cycling performances of the cathodes were investigated by galvanostatic discharge-charge  
203 cycling (GC) using an Arbin LBT-21084 battery tester at room temperature. Galvanostatic  
204 discharge-charge tests were carried out in the potential interval 1.8 - 2.6 V vs.  $\text{Li}^+/\text{Li}^0$  at different  
205 current rates. The C-rate was calculated using the theoretical capacity of sulphur (1672 mAh  $\text{g}^{-1}$ ).  
206 For cyclic voltammetry (CV), the electrode potential was reversibly scanned between an extended  
207 range of potential from 1.7 to 2.8 V vs.  $\text{Li}^+/\text{Li}^0$  at 0.1  $\text{mV s}^{-1}$ .

208 The catalytic effect of  $\text{MoS}_2$  and PANI on polysulfide redox conversion reaction was elucidated  
209 by exchange current density obtained from LSV analysis with a  $\text{Li}_2\text{S}_6$  catholyte solution. In this  
210 case, the working electrode containing  $\text{MoS}_2$  or PANI, KJB and PVdF in the weight ratio of  
211 80:10:10 was directly casted on a gas diffusion layer (GDL) and a pure lithium disk was used as  
212 counter/reference electrode. The cell was assembled using a 0.3 M  $\text{Li}_2\text{S}_6$  solution directly prepared  
213 in LiTFSI (1 M) in DME:DIOX 1:1 v/v + 0.25 M  $\text{LiNO}_3$  electrolyte, mixing  $\text{Li}_2\text{S}$  and  $\text{S}_8$  in the  
214 weight ratio of 1:5. For comparison a reference electrode containing only KJB: PVdF (weight ratio  
215 of 90:10) was prepared and subjected to the same electrochemical test. The scan speed of the LSV  
216 experiment was set at 0.1  $\text{mV s}^{-1}$ , and the voltage range was limited to 30 mV from open-circuit  
217 voltage (OCV).

218

### 3. RESULTS AND DISCUSSION

#### 3.1. Morphological characterization of MoS<sub>2</sub>/PANI

PANI was synthesized from aniline in an intermediate oxidation state (degree of reduction:  $y = 0.5$ ), in order to obtain emeraldine salt state (Figure 1a), in which benzene and quinoid structural unit coexist, thus assuring the optimal conductivity of the polymer [45][47].

Successively, PANI was mixed with bare bulk MoS<sub>2</sub> and subjected to an ultra-sonication process overnight in order to obtain different composites, as depicted in Figure 2a.

*Please insert here Figure 1.*

FESEM morphological analysis of MoS<sub>2</sub>/PANI composites are shown in Figure 2. The morphology of commercial untreated MoS<sub>2</sub>, shows adhered and stacked sheets, by van der Waals forces. In figure 2b a wide number of stacked and compressed MoS<sub>2</sub> layers are clearly observable, showing few micrometres in length and hundreds of nanometres in thickness. On the contrary, pure emeraldine polyaniline powder appears irregular and composed of granular and flakes particles with sharp edges (Figure 2c and d). The PANI polymer fragments resulted firmly agglomerated as a consequence of the electrostatic forces. However, the structure is clearly porous, which means that active sites of PANI are easily accessible by the electrolyte and polysulfides species. Regarding the composite samples, MoS<sub>2</sub>:PANI 3:7 shows highly compact structure with dimension and shape similar to the ones observed for pure PANI. Moreover, some well exfoliated MoS<sub>2</sub> nanosheets can be clearly identified (Figure e and f). The morphology of MoS<sub>2</sub>:PANI 7:3 composite appears less

compact, and the presence of the individual MoS<sub>2</sub> sheets is predominant as expected (Figure g and h).

*Please insert here Figure 2.*

X-ray-diffraction (XRD) patterns of as-prepared MoS<sub>2</sub>/PANI composites are shown in Figure 3a. The XRD pattern of bare bulk MoS<sub>2</sub> well matches with JCPDS (77-1716) of polycrystalline MoS<sub>2</sub>. The bare MoS<sub>2</sub> sample shows predominant peaks at 14.5°, 32.7°, 39.7°, 49.9°, 58.4°, 60.6°, 72.7° corresponding to the (002), (100), (103), (105), (110), (008) and (203) crystallographic planes respectively [48]. PANI emeraldine salt shows the presence of crystalline phase with two peaks at 20.0° and 25.1° which correspond to (020) and (200) planes of pure PANI, revealing parallel and perpendicular periodicity of the polymer chains [45][49]. Concerning the composites, both samples show the typical peaks of pure MoS<sub>2</sub> samples, but in the XRD pattern of MoS<sub>2</sub>:PANI 3:7 the two main peaks of PANI are still visible, confirming the presence of both compounds.

Raman spectroscopy, performed to assess the functionality and the intrinsic oxidation states of composites, is reported in Figure 3b. The peak at 1167 cm<sup>-1</sup> corresponds to the in-plane C-H bending of benzene or quinoid units, which is particularly evident when acid doping takes place. A second characteristic peak is observable at 1340 cm<sup>-1</sup>. This band is typically seen when quinoid rings convert to benzenoid rings, providing information about the delocalized polaronic structures vibrations of the PANI [50]. In particular, it is attributable to the radical cation (C-N<sup>+</sup> stretching mode) as consequence of PANI protonation and/or oxidation after acid or complexation treatment. The intense peak observed at 1610 cm<sup>-1</sup> is assigned to C=C stretching vibrations mode in quinoid ring. The shift of this peak, generally observable at 1592 cm<sup>-1</sup>, is attributable to the doped nature of

263 polyaniline [51]. Less pronounced peaks at 1491, 1418 and 1219  $\text{cm}^{-1}$ , are ascribable to the C=N,  
264 C=C stretching of the quinoid units, and C-N stretching of benzenoid units, respectively  
265 [29][50][51]. The Raman spectrum of commercial  $\text{MoS}_2$  powders confirms that the material is in  
266 bulk form. The  $E_{2g}^1$  peak, located at 383.4, is due to in-plane vibration modes of the S atoms, while  
267  $A_{1g}$  peak located at 407.5  $\text{cm}^{-1}$  is due to out-of-plane vibration modes of S atoms. The peaks  
268 position is layer dependent, and varies according to the number of stacked layers. Typically,  $E_{2g}^1$   
269 moves towards lower frequencies while  $A_{1g}$  shows a shift towards higher frequencies as the number  
270 of layers increases [52][53][54]. In the composite containing higher amounts of PANI, it is possible  
271 to notice a signal at about 400  $\text{cm}^{-1}$  which could be associated to  $\text{MoS}_2$ , in addition to the typical  
272 peaks linked to the emeraldine form of PANI. Concerning the composite containing higher amount  
273 of  $\text{MoS}_2$ , the two peaks ascribable to molybdenum disulphide can be prevalently seen, while the  
274 typical signals of emeraldine form are observed at higher wavelength [50].

275 The samples were also characterized by FTIR/ATR spectroscopy (Figure 3c and d). In the  
276 samples containing PANI, the adsorption bands at 1626 and 1521  $\text{cm}^{-1}$  are assigned to N-H bending  
277 of amine and C=C stretching vibrations of the quinonoid and benzenoid ring, respectively. In the  
278 region between 1200 and 1400  $\text{cm}^{-1}$  the C-N stretching modes of aromatic amine group are  
279 observable, while the peak at 1196  $\text{cm}^{-1}$  is ascribable to the vibrational mode band of  $Q=N^+H=B$  or  
280  $B-NH-B$ , typical for PANI doped structure [16]. These results clearly indicate the presence of  
281 PANI in its doped emeraldine state in all the  $\text{MoS}_2/\text{PANI}$  composites.

282

283 *Please insert here Figure 3.*

284

285 To evaluate the LiPSs adsorption capability 20  $\mu$ L of 1.0 mM of  $\text{Li}_2\text{S}_6$  solution diluted in 2 mL of  
286 DME:DIOX 1:1 v/v mixture were respectively added to 50 mg of  $\text{MoS}_2$ , PANI,  $\text{MoS}_2$ :PANI 3:7  
287 and  $\text{MoS}_2$ :PANI 7:3 (Figure SI1). After resting the samples for 12 hours, all the solutions showed  
288 colour fading, demonstrating an interaction with  $\text{Li}_2\text{S}_6$  (Figure SI1a).

289 In order to confirm the interaction between  $\text{MoS}_2$ , PANI and their combination with LiPSs, an  
290 UV-Vis absorption experiment was performed (Figure SI1b). Observing the UV-Vis spectra  
291 comparison, in the range between 350 – 500 nm, the solution containing the synthesized materials  
292 shows a remarkable absorption intensity decrease, which is consistent with the colour fading  
293 observed in the solutions after 12 h. In fact  $\text{Li}_2\text{S}_4$ ,  $\text{Li}_2\text{S}_6$  and  $\text{Li}_2\text{S}_8$  species produce characteristic  
294 peaks in the region above 300 nm, respectively at 400, 430, and around 500 nm [55][56][57], while  
295 elemental sulphur exhibits strong absorption below 300 nm [58][59]. These suggest the effective  
296 and enhanced LiPSs entrapment capability of  $\text{MoS}_2$  and PANI based materials.

297

### 298 **3.3. Electrochemical characterization**

299 The electrochemical performances of cathodes containing different double-layer coatings were  
300 examined by cyclic voltammetry in the voltage range of 1.7 – 2.8 V with a scan rate of 0.1  $\text{mV s}^{-1}$   
301 (Figure SI2a). The CV curve comparison, related to the first cycle, is depicted in Figure 4a.

302 Single-layer and double layer electrodes exhibit the characteristic reduction/oxidation peaks of S.  
303 More in detail, the cathodic scans exhibit two pronounced peaks corresponding to the reduction of  
304 elemental sulphur ( $\alpha\text{-S}_8$ ) to long chain lithium polysulfides  $\text{Li}_2\text{S}_x$  ( $4 < x < 8$ ) and the consequent  
305 reduction of long-chain polysulfides to solid  $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ .

306 A comparison of the voltammograms points out that the first reduction peak shape is similar for  
307 all the samples. The reaction starts at 2.39 V for all cathodes, except the DL-PANI one, for which  
308 the reaction starts at higher voltage (2.45 V). Concerning the peak position, SL and DL electrodes  
309 are superimposed at around 2.20 V, small shifts at 2.22V are seen for DL-MoS<sub>2</sub> and DL-  
310 MoS<sub>2</sub>:PANI 7:3. The second reduction starts at the same potential (2.07 V) for all the samples. DL-  
311 PANI shows similar shape to SL cathode but higher intensity, while the peak position of DL-MoS<sub>2</sub>  
312 is slightly shifted at higher potential (1.97 V) and less pronounced. Similarly, for the mixed DL, the  
313 peaks appear broader and shifted at lower potential (1.89 and 1.88 V for DL-MoS<sub>2</sub>:PANI 3:7 and  
314 DL-MoS<sub>2</sub>:PANI 7:3, respectively). An interesting aspect is that the curve profile of the two  
315 composites seem to be deriving from the combination of the profiles of DL electrodes containing  
316 either pure PANI or pure MoS<sub>2</sub>. This behaviour can be deducible observing the intermediate  
317 intensity of the peaks and the clear presence of shoulders in the DL composites profiles.

318 It is worth noting that the reduction and oxidation peaks for DL electrodes show a positive and  
319 negative shift, respectively, indicating improved redox kinetics of polysulfides conversion, as  
320 depicted in the zoomed image of Figure 4a.

321 At the 5<sup>th</sup> cycle (Figure 4b), CV profiles show slight shifts. Particularly, the first reduction peak of  
322 the SL standard cathode shows a shift at higher voltages, while the DL cathodes containing PANI  
323 show a shift for the second reduction peak. On the contrary DL cathode containing pure MoS<sub>2</sub> does  
324 not show any evident peak shift.

325 For all the cathodes, the peaks appear overlapped with a comparable intensity in all subsequent  
326 cycles, thanks to a stable and reversible electrochemical reaction (Figure SI2a). The differences  
327 observed between the first and the following cycles can be reasonably associated to a rearrangement  
328 and distribution of active sulphur [60].



*Please insert here Figure 4.*

To better discern peaks and related shoulders positions 1<sup>st</sup> and 2<sup>nd</sup> order derivative were calculated respectively for the anodic and cathodic branch of the first cycle, for all the samples, as reported in Table 1 and Figure SI3a,b.

Observing the voltammograms of all the cathodes, both cathodic peaks show at least two shoulders (Figure SI2a). In particular, the first cathodic peak shows one shoulder at higher potential (range: 2.25 – 2.31 V) and a second shoulder at lower potential (range: 2.16 – 2.19 V). At the same time, the second cathodic peak presents two shoulders, in the ranges of 2.01 – 2.03 and 1.87 – 1.94 V, respectively. It is important to note that the two mixed DL electrodes show additional shoulders in the range of 1.76 – 1.80 V. As widely reported, the presence of different peaks/shoulders are assigned to the different reduction reactions of the discharge (Figure SI2b). In particular, the process at higher voltages can be related to  $\alpha$ -S<sub>8</sub> ring opening and the consequent formation and reduction of long chain lithium polysulfides (Li<sub>2</sub>S<sub>x</sub>, 4 < x < 8). While the second reduction peak and the related shoulders are attributable to soluble high order LiPSs that are converted to short chain lithium polysulfides (Li<sub>2</sub>S<sub>x</sub>, 1 < x < 4) and consequently to final Li<sub>2</sub>S. It is worth noting that, during the different processes, disproportionation reactions occur resulting in the simultaneous coexistence of multiple species [61], even if Li<sub>2</sub>S<sub>6</sub> and Li<sub>2</sub>S<sub>4</sub> are generally reported as the most stable intermediate polysulfides [62]. The presence of evident and well-defined shoulders for the DL electrodes containing both PANI and MoS<sub>2</sub>, suggests that the concomitant presence of these materials shift and emphasises some reactions. This typical behaviour can be due to the physico-chemical interaction of lithium polysulfides with PANI and/or MoS<sub>2</sub>.

352 In the subsequent anodic scan, only one broad oxidation peak, located in the potential range of 2.2  
353 – 2.6 V, is clearly seen. Comparing the CVs, the oxidation reaction of all DL electrodes starts at  
354 lower potential, at around 2.16 V instead of 2.25 V (observed for SL electrode). Concerning the  
355 peaks shape and position, DL electrodes show visible shifts at higher voltages, as a consequence of  
356 broader profiles. A broader profile indicates the presence of numerous species, which undergo  
357 oxidation, over a wide range of potentials. In this case also, the 1<sup>st</sup> order derivative allows to  
358 identify the correct peaks position (Figure SI3a). The SL electrode shows a peak at lower potential  
359 (2.44 V), while all the DL electrodes show a shift at higher potential, at 2.58, 2.50, 2.52 and 2.52 for  
360 DL-PANI, DL-MoS<sub>2</sub>, DL-MoS<sub>2</sub>:PANI 3:7 and DL-MoS<sub>2</sub>:PANI 7:3, respectively. At the same time,  
361 the 2<sup>nd</sup> order derivative curve allows to identify the inflection points of the voltammograms, located  
362 in correspondence to the peak shoulders (Figure SI3b). The SL electrode shows two shoulders at  
363 lower (2.37 V) and higher (2.55 V) voltages than the main peak. The same inflection points were  
364 found for the DL electrodes, but slightly shifted, as reported in Table 1. Two additional inflection  
365 points are reported for DL electrodes. In particular, the DL electrodes containing pure PANI and  
366 MoS<sub>2</sub>:PANI 3:7 show a shoulder at around 2.63 V, while DL with pure MoS<sub>2</sub> and MoS<sub>2</sub>:PANI 7:3  
367 show a shoulder at lower voltage, around 2.44 V. These processes, occurring in the range of 2.45 –  
368 2.64 V, are typical of the oxidation reaction of medium-chain polysulfides to long chain  
369 polysulfides. While the reaction occurring at lower voltages (2.37 V) is related to short chain  
370 polysulfides conversion to medium chain polysulfides species.

371 Generally, the broader shape observed for the DL electrodes is due to the presence of the second  
372 layer and to the consequent smaller ion diffusion typical of thicker electrodes [63]. But in this case  
373 the different peak shape can be strictly related to the different amount of each single component  
374 (MoS<sub>2</sub> and PANI) in the double layer. This is clear in the CV of cathodes containing the two

375 materials in different proportions, where the contribution of each single component is easily  
 376 detectable.

377

378 **Table 1.** 1<sup>st</sup> and 2<sup>nd</sup> order derivative for the first anodic and cathodic branch of cyclic  
 379 voltammetry, for all the samples.

380

		SL	DL-PANI	DL-MOS <sub>2</sub>	DL- MOS <sub>2</sub> :PANI 3:7	DL- MOS <sub>2</sub> :PANI 7:3
<i>Cycle 1</i>		<i>Cathodic</i>				
<b>δI/δE</b> <b>(A V<sup>-1</sup>)</b>	Peak 1	2.20	2.20	2.22	2.20	2.22
	Peak 2	1.95	1.92	1.97	1.89	1.88
<b>δ<sup>2</sup>I/δE<sup>2</sup></b> <b>(A V<sup>-2</sup>)</b>	Peak 1	2.25	2.25	2.31	2.28	2.31
	Peak 2	2.16	2.17	2.19	2.16	2.18
	Peak 3	2.03	2.03	2.02	2.01	2.02
	Peak 4	1.89	1.87	1.93	1.94	1.93
	Peak 5	-	-	-	1.79	1.80
	Peak 6					1.76
<i>Cycle 1</i>		<i>Anodic</i>				
<b>δI/δE</b> <b>(A V<sup>-1</sup>)</b>	Peak 1	2.44	2.58	2.50	2.52	2.52

$\delta^2 I / \delta E^2$ (A V <sup>-2</sup> )	Peak 1	2.37	2.37	2.35	2.36	2.36
	Peak 2	2.55	2.54	2.55	2.58	2.59
	Peak 3	-	2.63		2.66	
	Peak 4			2.44		2.46

381

382

383 The electrochemical behaviour of pure MoS<sub>2</sub> and pure PANI was also investigated in the voltage  
384 range 1.6 – 2.8 V. Since no peaks are observed, it is possible to assume a negligible contribution of  
385 PANI and MoS<sub>2</sub> in the investigated voltage range (Figure SI4).

386 This behaviour suggests that the peaks shift, observed for all the DL cathodes, cannot be simply  
387 correlated to the smaller ion diffusion and lower electrolyte permeability, because they show  
388 comparable or lower polarization respect to the single-layer electrode, as also visible in  
389 charge/discharge curves reported below.

390 The double-layer contribution, and the consequent role of different ratio of MoS<sub>2</sub> and PANI, is  
391 further evaluated by long cycling stability at C/5 for more than 500 cycles (Figure 5).

392 In general DL electrodes deliver a considerably higher specific capacity if compared to SL  
393 electrode. The initial specific capacity of the SL cathode is 750 mAh g<sup>-1</sup>. DL cathodes containing  
394 pure MoS<sub>2</sub>, pure PANI, MoS<sub>2</sub>:PANI 3:7 and MoS<sub>2</sub>:PANI 7:3 deliver 1100, 1450, 1180, and 1240  
395 mAh g<sup>-1</sup> respectively, at C/10 (Figure 5a). The higher capacity obtained at the first cycle means that  
396 sulphur is exploited more efficiently in DL electrodes than in SL, thanks to an improved electronic  
397 conductivity [64]. The specific capacity of DL electrodes is maintained above 600 mAh g<sup>-1</sup> at C/5  
398 for more than 300 cycles which is almost 30 % higher than that of the SL electrode. In fact, the

specific capacity of SL cathode drops to 440 mAh g<sup>-1</sup> after 400 cycles, showing a capacity decay of 0.53 % per cycle, and after 450 cycles the electrode shows pronounced shuttling effect. All the DL electrodes show better cycling stability, benefiting from PANI and MoS<sub>2</sub> coating. DL containing pure PANI shows a specific capacity of 355 mAh g<sup>-1</sup>, DL with pure MoS<sub>2</sub> shows a higher specific capacity of about 480 mAh g<sup>-1</sup>, while the two DLs containing a mixture of MoS<sub>2</sub> and PANI show a specific capacity close to 600 mAh g<sup>-1</sup> after more than 500 cycles at C/5 (Figure 5a). The superior cycle stability of double-layer cathodes containing both the additive materials is probably due to the enhanced electrical conductivity provided by PANI framework and physical confinement of polysulfides along with fast redox reaction ascribable to MoS<sub>2</sub> [65].

The capacity retention, calculated considering the initial cycle at C/10 and the first cycle at the same current regime after 500 cycles, is about 44 % for SL cathode, while it is 35, 50, 57, 56 % for DL containing PANI, MoS<sub>2</sub>, MoS<sub>2</sub>:PANI 3:7 and MoS<sub>2</sub>:PANI 7:3, respectively. Concerning higher C-rates (*e.g.* C/5) the capacity retention is 49 % for the SL and 40, 61, 58 and 61 % for PANI, MoS<sub>2</sub>, MoS<sub>2</sub>:PANI 3:7 and MoS<sub>2</sub>:PANI 7:3, respectively.

As reported in Figure SI5, the coulombic efficiency (CE) is quickly stabilized above 95 % for all the cathodes, excluding the DL containing pure PANI, for which it is less than 90 % after 500 cycles. The presence of PANI slightly affects the coulombic efficiency of DL cathodes with mixed compounds, confirming that CE is increased and stabilized by the presence of MoS<sub>2</sub>.

The corresponding discharge-charge voltage profiles (Figure 5b) display two typical discharge plateaus in agreement with the two main couple of peaks observed in the CV curves. In general, DL electrodes show flat and stable plateaus with lower polarization if compared to SL electrode. In contrast to the other samples, the DL cathode containing pure MoS<sub>2</sub> shows less flat discharge profile, and a third plateau is detectable at lower voltage. The third plateau is particularly evident increasing the cycle number and evolves in a linear voltage drop in the fifth cycle. This behaviour

423 was already observed in previous work adopting MoS<sub>2</sub> in lithium sulphur systems [44].  
424 Nevertheless, the charge curve profile is similar for all the samples, showing only the two typical  
425 oxidation reaction plateaus.

426 The voltage hysteresis between charge and discharge curves confirms a higher overpotential for  
427 the SL electrode (Figure 5c). Analysing the voltage hysteresis for the 5<sup>th</sup> cycle (C/5), SL cathode  
428 shows higher  $\Delta E$  value (265 mV), followed by DL-PANI (264 mV), DL-MoS<sub>2</sub>:PANI 3:7 (251 mV),  
429 DL-MoS<sub>2</sub>:PANI 7:3 (219 mV) and DL-MoS<sub>2</sub> (216 mV). The voltage hysteresis trend of DL  
430 electrodes, especially at higher C-rates, points out the active role of MoS<sub>2</sub> in promoting polysulfides  
431 conversion reaction.

432 The lower polarization of DL electrodes is further highlighted by means of the corresponding  
433 capacity derivative-voltage profiles ( $dQ/dV$  vs  $V$ ), as shown in Figure 5d and Figure SI6. The  
434 picture clearly shows the lower overpotential for all DL electrodes, particularly in the anodic  
435 branch.

436 The derivative-voltage profiles comparison of different cycles at C/5 (Figure SI6b), demonstrate  
437 higher reversibility of the process for the two mixed DL.

438 The  $dQ/dV$  vs  $V$  profiles at higher cycle number at C/5 (Figure SI6b) it is important to note that  
439 the presence of PANI in the double layer induces a higher contribution to the lower voltage  
440 reduction reaction due to the reversible conversion reaction of short-chain polysulfides to LiS<sub>2</sub> final  
441 product. On the contrary, the contribution of MoS<sub>2</sub> seems more pronounced to higher voltage  
442 reduction reaction, which involves the long-chain polysulfides conversion to short-chain species.  
443 The trend is confirmed in the anodic branch, but increasing the number of cycles a balancing of the  
444 two contributions is observed. This behaviour confirms the different active role of both components

445 in the DL electrodes and their synergic effect on polysulfides conversion. In general, the derivative-  
446 voltage profiles comparison, confirms higher process reversibility for the mixed DL.

447 To better evaluate the role of additives that are present in the double-layer, the capacity  
448 contribution from upper-plateau discharge capacity (Q1) and lower-plateau discharge capacity (Q2)  
449 was separated and quantified. In fact, quantification of Q1 at low C-rates (*e.g.* C/10), is an  
450 important parameter because it is directly imputable to long-chain polysulfides formation.

451 As reported in Figure 5e, Q1 is sensibly lower than Q2, representing less than 45 % of the total  
452 discharge capacity up to the 500<sup>th</sup> cycle, for all the cathodes. More in detail, for the first three cycles  
453 at C/10, the Q1 contribution to the total capacity is close to 40 % for the SL cathode while it is less  
454 than 36 % for all the DL cathodes. On the contrary Q2 of DL electrodes, which is due to short-chain  
455 polysulfides conversion, is higher than 65 % and still remains higher than 60 % at C/5 after 500  
456 cycles.

457 At the same time, the ratio between the lower and the upper plateau capacity (Q2/Q1) is a useful  
458 parameter to estimate the Li<sub>2</sub>S deposition efficiency (Figure 5f). In the first three cycles, Q2/Q1 is  
459 lower for the SL cathode (1.61) and higher for all the DL cathodes, in particular for the one with  
460 MoS<sub>2</sub>. In the following cycles at C/5, Q2/Q1 is higher for all the DL cathodes in comparison to the  
461 SL one, this means that the presence of MoS<sub>2</sub> and PANI, or their combination, improves the  
462 efficiency of the conversion reaction of polysulfides to Li<sub>2</sub>S, for more than 500 cycles. It is  
463 important to note that the lower Q2/Q1 value, obtained for SL at 500<sup>th</sup> cycle, is not representative  
464 because shuttle phenomenon occurs in the electrode after 450 cycles, and it is reported in the picture  
465 only for completeness.

466 To further discriminate the catalytic effect of MoS<sub>2</sub> and PANI in the double-layer with different  
467 ratio, Tafel plots were obtained from LSV analysis, and the exchange current density values were

468 evaluated. As shown in Figure 5g, Tafel plots of pure MoS<sub>2</sub> and pure PANI electrodes were  
469 constructed for the anodic and cathodic processes. The anodic/cathodic exchange current density  
470 are  $1.4/2.4 \times 10^{-4}$ ,  $3.8/3.7 \times 10^{-1}$  and  $1.8/2.7 \times 10^{-3}$  mA cm<sup>-2</sup> for KJB, MoS<sub>2</sub> and PANI, respectively.  
471 These values prove the accelerated conversion of LiPS due to the presence of MoS<sub>2</sub>, a lower  
472 catalytic effect of PANI and the inconspicuous role of KJB.

473 These results confirm that MoS<sub>2</sub> can chemically immobilize polysulfides [66] but also promote  
474 the redox reaction kinetics of polysulfides conversion at solid-liquid interphase, as already reported  
475 [67][68][69]. In particular, Sun *et al.* suggested that MoS<sub>2</sub> can spatially regulate the deposition of  
476 Li<sub>2</sub>S, generating a large number of reaction sites with accelerated electron transport [70]. On the  
477 other side, the contribution of PANI chains can be explained by the presence of typical  
478 electropositive amine and imine groups of emeraldine salt which can interact with polysulfides  
479 through electrostatic forces, reducing the displacement of sulphur during cycling [40][71]. The  
480 rough surface of PANI agglomerates also creates higher contact area between electrolyte and  
481 sulphur particles, giving to the electrode more mechanical flexibility and alleviating the stress  
482 caused by volume change during charge/discharge process [71][72][73].

483

484 *Please insert here Figure 5.*

485

486 The role of the two compounds was also evaluated by a morphological point of view. Figure 6  
487 shows the FESEM image of standard SL and DL electrodes. The micrographs of SL electrode  
488 (Figure 5a,b) clearly reveal some protuberances attributable to the presence of sulphur agglomerates  
489 covered by KJB nanoparticles. DL with pure PANI (Figure 6c,d) shows a porous structure, as  
490 consequence of polymer morphology, as observed in Figure 2. On the contrary, the surface of the



491 electrode with pure MoS<sub>2</sub> (Figure 6e,f) appears smoother with few cracks, meaning that the  
492 presence of MoS<sub>2</sub> helps to achieve a more compact structure of the double-layer. The same  
493 consideration can be done comparing the DL electrodes with a mixture of PANI and MoS<sub>2</sub>: the  
494 sample containing excess of PANI (Figure 6g,h) presents an electrode surface rich of pores and  
495 cracks, while the electrode containing a higher amount of MoS<sub>2</sub> (Figure 6i,j) shows a smooth and  
496 compact structure. In both samples MoS<sub>2</sub> and PANI are homogeneously distributed on the surface.

497

498 *Please insert here Figure 6.*

499

500 In conclusion, the 3D framework originated by the mixing of the two compounds provides fast  
501 electrons and ions transport pathways during the electrochemical process. In DL electrodes the  
502 combination of MoS<sub>2</sub> and PANI is able to trap polysulfide species inside the top layer, thus  
503 alleviating the shuttle effect thanks to the synergic contribution of the two compounds. In addition,  
504 the use of a second layer increases the volume available for sulphur and lithium polysulfides  
505 accommodation, preserving the electrolyte infiltration and enabling the movement of lithium ions  
506 [46] as depicted in Figure 7.

507

508 *Please insert here Figure 7.*

509

510

511

512

513

514

515

516

#### 4. CONCLUSIONS

In summary, we investigated the ability of MoS<sub>2</sub> and PANI, both individually and together, to adsorb LiPSs, preventing polysulfides dissolution and accelerating the redox reaction kinetics of polysulfides conversion thus enhancing the performances of the lithium sulphur battery.

In particular, MoS<sub>2</sub> and PANI composites were obtained by a direct ex-situ synthesis, avoiding long and complex procedure. At the same time, to evaluate the synergy effect of the two materials, a simple double-layer approach was used, directly coating the surface of a standard sulphur cathode with a second layer containing different amounts of MoS<sub>2</sub> and PANI.

In this way, we demonstrated that the top-layer provides an integrated conductive pathway for electrons, due to the presence of PANI, which also acts as physical barrier for polysulfides migration. At the same time, the presence of MoS<sub>2</sub> induces a catalytic effect on the LiPSs conversion reaction, improving the electrochemical performances of the cathode.

In particular, the implementation of DL-MoS<sub>2</sub>:PANI 7:3 noticeably improved the electrochemical behaviour of the sulphur cathode, showing a final specific capacity close to 600 mAh g<sup>-1</sup>, 42 % higher than the standard sulphur cathode, after 500 cycles.

Therefore, the use of MoS<sub>2</sub>/PANI second layer on a sulphur cathode has a great potential to enhance the electrochemical performances of Li-S batteries. Moreover, the easy preparation and implementation represent a possible solution for future up-scaling.

#### Acknowledgments

538 The authors want to thank ERASMUS+ programme of Politecnico di Torino and FEDER through  
539 the COMPETE 2020 Programme, and the FCT—Fundação para a Ciência e a Tecnologia, I.P.,  
540 under the scope of the project UIDB/50025/2020 for funding.

541

542

### 543 Captions to Figures

544 **Fig. 1.** Polymerization scheme of aniline emeraldine salt chains (a), schematic illustration of the  
545 MoS<sub>2</sub>/PANI assembly (b).

546 **Fig. 2.** FESEM micrographs of: bare MoS<sub>2</sub> (a,b), bare PANI (c,d), MoS<sub>2</sub>:PANI 3:7 (e,f) and  
547 MoS<sub>2</sub>:PANI 7:3 (g,h).

548 **Fig. 3.** XRD spectra of bare MoS<sub>2</sub>, bare PANI, MoS<sub>2</sub>:PANI 3:7, and MoS<sub>2</sub>:PANI 7:3 (a from top to  
549 bottom), Raman spectra comparison (b), FTIR/ATR spectra comparison (c) and zoomed area of  
550 interest (d).

551 **Fig. 4.** Cyclic voltammogram comparison (a), and zoomed area (b) of the first cycle and of the fifth  
552 cycle (c) scan rate 0.1 mV s<sup>-1</sup>, in the range 1.6 – 2.8 V.

553 **Fig. 5.** Comparison of the specific capacity vs. cycle number at C/5 (a), comparison of  
554 charge/discharge voltage profiles for the first cycle at C/10 (d), and for the fifth cycle at C/5 (c),  
555 plot of dQ/dV vs. V reproduced from the 5<sup>th</sup> charge–discharge curves at C/5 (d), Q1% comparison  
556 (e) and Q1/Q2 ratio (f) for different cycles, Tafel plots of the Li<sub>2</sub>S<sub>6</sub> solution redox on PANI or  
557 MoS<sub>2</sub> materials, derived from LSV scans (g).

558 **Fig. 6.** FESEM micrographs of different cathodes: SL standard cathode (a,b), DL-PANI (c,d), DL-  
559 MoS<sub>2</sub> (e,f), DL-MoS<sub>2</sub>:PANI 3:7 (g,h) and DL-MoS<sub>2</sub>:PANI 7:3 (i,j).

560 **Fig. 7.** Schematic representation of double-layer cathode electrode.

561 **References:**

562

- 563 [1] A.N. Mistry, P.P. Mukherjee, ‘Shuttle’ in Polysulfide Shuttle: Friend or Foe?, *J. Phys. Chem.*  
564 *C.* 122 (2018) 23845–23851. <https://doi.org/10.1021/acs.jpcc.8b06077>.
- 565 [2] W. Kang, N. Deng, J. Ju, Q. Li, D. Wu, X. Ma, L. Li, M. Naebe, B. Cheng, A review of  
566 recent developments in rechargeable lithium-sulfur batteries, *Nanoscale.* 8 (2016) 16541–  
567 16588. <https://doi.org/10.1039/c6nr04923k>.
- 568 [3] B. Jin, J.U. Kim, H.B. Gu, Electrochemical properties of lithium-sulfur batteries, *J. Power*  
569 *Sources.* 117 (2003) 148–152. [https://doi.org/10.1016/S0378-7753\(03\)00113-7](https://doi.org/10.1016/S0378-7753(03)00113-7).
- 570 [4] H. Lin, L. Yang, X. Jiang, G. Li, T. Zhang, Q. Yao, G.W. Zheng, J.Y. Lee, Electrocatalysis  
571 of polysulfide conversion by sulfur-deficient MoS<sub>2</sub> nanoflakes for lithium-sulfur batteries,  
572 *Energy Environ. Sci.* 10 (2017) 1476–1486. <https://doi.org/10.1039/c7ee01047h>.
- 573 [5] N. Jayaprakash, J. Shen, S.S. Moganty, A. Corona, L.A. Archer, Porous hollow  
574 carbon@sulfur composites for high-power lithium-sulfur batteries, *Angew. Chemie - Int. Ed.*  
575 50 (2011) 5904–5908. <https://doi.org/10.1002/anie.201100637>.
- 576 [6] X.B. Cheng, R. Zhang, C.Z. Zhao, Q. Zhang, Toward Safe Lithium Metal Anode in  
577 Rechargeable Batteries: A Review, *Chem. Rev.* 117 (2017) 10403–10473.  
578 <https://doi.org/10.1021/acs.chemrev.7b00115>.
- 579 [7] V.S. Kolosnitsyn, E. V. Karaseva, Lithium-sulfur batteries: Problems and solutions, *Russ. J.*  
580 *Electrochem.* 44 (2008) 506–509. <https://doi.org/10.1134/S1023193508050029>.
- 581 [8] A. Manthiram, Y. Fu, S. Chung, C. Zu, Y. Su, Rechargeable Lithium – Sulfur Batteries,  
582 (2014).
- 583 [9] Y. V Mikhaylik, J.R. Akridge, Polysulfide Shuttle Study in the Li/S Battery System, *J.*  
584 *Electrochem. Soc.* 151 (2004) A1969. <https://doi.org/10.1149/1.1806394>.
- 585 [10] L. Tan, X. Li, Z. Wang, H. Guo, J. Wang, Lightweight Reduced Graphene Oxide@MoS<sub>2</sub>  
586 Interlayer as Polysulfide Barrier for High-Performance Lithium-Sulfur Batteries, *ACS Appl.*  
587 *Mater. Interfaces.* 10 (2018) 3707–3713. <https://doi.org/10.1021/acsami.7b18645>.

- 588 [11] J. Yan, X. Liu, B. Li, Capacity Fade Analysis of Sulfur Cathodes in Lithium – Sulfur  
589 Batteries, (2016). <https://doi.org/10.1002/advs.201600101>.
- 590 [12] A. Manthiram, Y. Fu, Y.-S. Su, Challenges and Prospects of Lithium–Sulfur Batteries, *Acc.*  
591 *Chem. Res.* 46 (2013) 1125–1134. <https://doi.org/10.1021/ar300179v>.
- 592 [13] X. Xie, Z. Ao, D. Su, J. Zhang, G. Wang, MoS<sub>2</sub>/graphene composite anodes with enhanced  
593 performance for sodium-ion batteries: The role of the two-dimensional heterointerface, *Adv.*  
594 *Funct. Mater.* 25 (2015) 1393–1403. <https://doi.org/10.1002/adfm.201404078>.
- 595 [14] Z.A. Ghazi, X. He, A.M. Khattak, N.A. Khan, B. Liang, A. Iqbal, J. Wang, H. Sin, L. Li, Z.  
596 Tang, MoS<sub>2</sub>/Celgard Separator as Efficient Polysulfide Barrier for Long-Life Lithium-  
597 Sulfur Batteries, *Adv. Mater.* 29 (2017) 1606817. <https://doi.org/10.1002/adma.201606817>.
- 598 [15] Y. Luo, R. Guo, T. Li, F. Li, Z. Liu, M. Zheng, B. Wang, Z. Yang, H. Luo, Y. Wan,  
599 Application of Polyaniline for Li-Ion Batteries, Lithium–Sulfur Batteries, and  
600 Supercapacitors, *ChemSusChem.* 12 (2019) 1591–1611.  
601 <https://doi.org/10.1002/cssc.201802186>.
- 602 [16] Y. Yao, H. Zhang, X. Wang, Polyaniline: an effective suppressor against diffusion and  
603 dissolution of polysulfides in Li-S battery, *J. Solid State Electrochem.* 23 (2019) 2559–2567.  
604 <https://doi.org/10.1007/s10008-019-04340-3>.
- 605 [17] J. Wu, F. Ciucci, J.-K. Kim, Molybdenum Disulfide Based Nanomaterials for Rechargeable  
606 Batteries, *Chem. – A Eur. J.* 26 (2020) 6296–6319.  
607 <https://doi.org/https://doi.org/10.1002/chem.201905524>.
- 608 [18] Y. Liu, C. Cui, Y. Liu, W. Liu, J. Wei, Application of MoS<sub>2</sub> in the cathode of lithium sulfur  
609 batteries, *RSC Adv.* 10 (2020) 7384–7395. <https://doi.org/10.1039/C9RA09769D>.
- 610 [19] L. Tan, X. Li, Z. Wang, H. Guo, J. Wang, Lightweight Reduced Graphene Oxide@MoS<sub>2</sub>  
611 Interlayer as Polysulfide Barrier for High-Performance Lithium–Sulfur Batteries, *ACS Appl.*  
612 *Mater. Interfaces.* 10 (2018) 3707–3713. <https://doi.org/10.1021/acsami.7b18645>.
- 613 [20] H. Althues, S. Dörfler, S. Thieme, P. Strubel, S. Kaskel, Sulfur Cathodes 2 . 1 Cathode  
614 Design Criteria, (2019).
- 615 [21] W. Yang, W. Yang, L. Dong, X. Gao, G. Wang, G. Shao, Enabling immobilization and

- conversion of polysulfides through a nitrogen-doped carbon nanotubes/ultrathin MoS<sub>2</sub> nanosheet core–shell architecture for lithium–sulfur batteries, *J. Mater. Chem. A*. 7 (2019) 13103–13112. <https://doi.org/10.1039/C9TA03227D>.
- [22] J. He, G. Hartmann, M. Lee, G.S. Hwang, Y. Chen, A. Manthiram, Freestanding 1T MoS<sub>2</sub>/graphene heterostructures as a highly efficient electrocatalyst for lithium polysulfides in Li–S batteries, *Energy Environ. Sci.* 12 (2019) 344–350. <https://doi.org/10.1039/C8EE03252A>.
- [23] M. Liu, C. Zhang, J. Su, X. Chen, T. Ma, T. Huang, A. Yu, Propelling Polysulfide Conversion by Defect-Rich MoS<sub>2</sub> Nanosheets for High-Performance Lithium–Sulfur Batteries, *ACS Appl. Mater. Interfaces*. 11 (2019) 20788–20795. <https://doi.org/10.1021/acsami.9b03011>.
- [24] H. Lin, S. Zhang, T. Zhang, H. Ye, Q. Yao, G.W. Zheng, J.Y. Lee, Simultaneous Cobalt and Phosphorous Doping of MoS<sub>2</sub> for Improved Catalytic Performance on Polysulfide Conversion in Lithium–Sulfur Batteries, *Adv. Energy Mater.* 9 (2019) 1902096. <https://doi.org/https://doi.org/10.1002/aenm.201902096>.
- [25] D. Liu, C. Zhang, G. Zhou, W. Lv, G. Ling, L. Zhi, Q.-H. Yang, Catalytic Effects in Lithium–Sulfur Batteries: Promoted Sulfur Transformation and Reduced Shuttle Effect, *Adv. Sci.* 5 (2018) 1700270. <https://doi.org/https://doi.org/10.1002/advs.201700270>.
- [26] X.L. Li, T.C. Li, S. Huang, J. Zhang, M.E. Pam, H.Y. Yang, Controllable Synthesis of Two-Dimensional Molybdenum Disulfide (MoS<sub>2</sub>) for Energy-Storage Applications, *ChemSusChem*. 13 (2020) 1379–1391. <https://doi.org/10.1002/cssc.201902706>.
- [27] Y. Cao, Y. Lin, J. Wu, X. Huang, Z. Pei, J. Zhou, G. Wang, Two-Dimensional MoS<sub>2</sub> for Li–S Batteries: Structural Design and Electronic Modulation, *ChemSusChem*. 13 (2020) 1392–1408. <https://doi.org/10.1002/cssc.201902688>.
- [28] Q. Zhang, X. Zhang, M. Li, J. Liu, Y. Wu, Sulfur-deficient MoS<sub>2</sub>-x promoted lithium polysulfides conversion in lithium-sulfur battery: A first-principles study, *Appl. Surf. Sci.* 487 (2019) 452–463. <https://doi.org/10.1016/j.apsusc.2019.05.138>.
- [29] M.-I. Boyer, S. Quillard, E. Rebourt, G. Louarn, J.P. Buisson, A. Monkman, S. Lefrant, Vibrational Analysis of Polyaniline: A Model Compound Approach, *J. Phys. Chem. B*. 102

- (1998) 7382–7392. <https://doi.org/10.1021/jp972652o>.
- [30] S. Moon, J.-K. Yoo, Y.H. Jung, J.-H. Kim, Y.S. Jung, D.K. Kim, Effective Suppression of Polysulfide Dissolution by Uniformly Transfer-Printed Conducting Polymer on Sulfur Cathode for Li-S Batteries, *J. Electrochem. Soc.* 164 (2017) A6417–A6421. <https://doi.org/10.1149/2.0621701jes>.
- [31] Q. Lu, H. Gao, Y. Yao, N. Liu, X. Wang, F. Wang, One-step synthesis of an urchin-like sulfur/polyaniline nano-composite as a promising cathode material for high-capacity rechargeable lithium–sulfur batteries, *RSC Adv.* 5 (2015) 92918–92922. <https://doi.org/10.1039/C5RA21550A>.
- [32] C.-Y. Chen, H.-J. Peng, T.-Z. Hou, P.-Y. Zhai, B.-Q. Li, C. Tang, W. Zhu, J.-Q. Huang, Q. Zhang, A Quinonoid-Imine-Enriched Nanostructured Polymer Mediator for Lithium–Sulfur Batteries, *Adv. Mater.* 29 (2017) 1606802. <https://doi.org/https://doi.org/10.1002/adma.201606802>.
- [33] C.-H. Chang, S.-H. Chung, A. Manthiram, Ultra-lightweight PANiNF/MWCNT-functionalized separators with synergistic suppression of polysulfide migration for Li–S batteries with pure sulfur cathodes, *J. Mater. Chem. A* 3 (2015) 18829–18834. <https://doi.org/10.1039/C5TA05053G>.
- [34] X. Hong, Y. Liu, Y. Li, X. Wang, J. Fu, X. Wang, Application progress of polyaniline, polypyrrole and polythiophene in lithium-sulfur batteries, *Polymers (Basel)* 12 (2020). <https://doi.org/10.3390/polym12020331>.
- [35] J. Jin, Z. Wen, G. Ma, Y. Lu, K. Rui, Mesoporous carbon/sulfur composite with polyaniline coating for lithium sulfur batteries, *Solid State Ionics* 262 (2014) 170–173. <https://doi.org/https://doi.org/10.1016/j.ssi.2013.09.060>.
- [36] X. Zhao, H.-J. Ahn, K.-W. Kim, K.-K. Cho, J.-H. Ahn, Polyaniline-Coated Mesoporous Carbon/Sulfur Composites for Advanced Lithium Sulfur Batteries, *J. Phys. Chem. C* 119 (2015) 7996–8003. <https://doi.org/10.1021/jp511846z>.
- [37] K. Zhang, Y. Xu, Y. Lu, Y. Zhu, Y. Qian, D. Wang, J. Zhou, N. Lin, Y. Qian, A graphene oxide-wrapped bipyramidal sulfur@polyaniline core–shell structure as a cathode for Li–S batteries with enhanced electrochemical performance, *J. Mater. Chem. A* 4 (2016) 6404–



- 674 6410. <https://doi.org/10.1039/C6TA01118G>.
- 675 [38] H. Deng, L. Yao, Q.-A. Huang, Q. Su, J. Zhang, F. Zhang, G. Du, Facile assembly of a  
 676 S@carbon nanotubes/polyaniline/graphene composite for lithium–sulfur batteries, *RSC Adv.*  
 677 7 (2017) 9819–9825. <https://doi.org/10.1039/C6RA28288A>.
- 678 [39] X. Li, M. Rao, D. Chen, H. Lin, Y. Liu, Y. Liao, L. Xing, W. Li, Sulfur supported by carbon  
 679 nanotubes and coated with polyaniline: Preparation and performance as cathode of lithium-  
 680 sulfur cell, *Electrochim. Acta.* 166 (2015) 93–99.  
 681 <https://doi.org/10.1016/j.electacta.2015.03.070>.
- 682 [40] X. Zhao, J.-K. Kim, H.-J. Ahn, K.-K. Cho, J.-H. Ahn, A ternary sulfur/polyaniline/carbon  
 683 composite as cathode material for lithium sulfur batteries, *Electrochim. Acta.* 109 (2013)  
 684 145–152. <https://doi.org/https://doi.org/10.1016/j.electacta.2013.07.067>.
- 685 [41] Y. Sun, S. Wang, H. Cheng, Y. Dai, J. Yu, J. Wu, Synthesis of a ternary  
 686 polyaniline@acetylene black-sulfur material by continuous two-step liquid phase for lithium  
 687 sulfur batteries, *Electrochim. Acta.* 158 (2015) 143–151.  
 688 <https://doi.org/https://doi.org/10.1016/j.electacta.2015.01.150>.
- 689 [42] M. Wang, W. Wang, A. Wang, K. Yuan, L. Miao, X. Zhang, Y. Huang, Z. Yu, J. Qiu, A  
 690 multi-core–shell structured composite cathode material with a conductive polymer network  
 691 for Li–S batteries, *Chem. Commun.* 49 (2013) 10263–10265.  
 692 <https://doi.org/10.1039/C3CC45412F>.
- 693 [43] U. Zubair, D. Versaci, M. Umer, J. Amici, C. Francia, S. Bodoardo, Lithium polysulfides  
 694 immobilization exploiting formate-ion doped polyaniline wrapped carbon for Long cycle life  
 695 sulfur cathodes via conventional electrode processing, *Mater. Today Commun.* 26 (2021)  
 696 101970. <https://doi.org/10.1016/j.mtcomm.2020.101970>.
- 697 [44] P. Guo, D. Liu, Z. Liu, X. Shang, Q. Liu, D. He, Dual functional MoS<sub>2</sub>/graphene interlayer  
 698 as an efficient polysulfide barrier for advanced lithium-sulfur batteries, *Electrochim. Acta.*  
 699 256 (2017) 28–36. <https://doi.org/10.1016/j.electacta.2017.10.003>.
- 700 [45] M.L. Para, D. Versaci, J. Amici, M.F. Caballero, M.V. Cozzarin, C. Francia, S. Bodoardo,  
 701 M. Gamba, Synthesis and characterization of montmorillonite/polyaniline composites and its  
 702 usage to modify a commercial separator, *J. Electroanal. Chem.* 880 (2021) 114876.

- 703 <https://doi.org/10.1016/j.jelechem.2020.114876>.
- 704 [46] X. Zhao, H.J. Ahn, K.W. Kim, K.K. Cho, J.H. Ahn, Polyaniline-coated mesoporous  
705 carbon/sulfur composites for advanced lithium sulfur batteries, *J. Phys. Chem. C*. 119 (2015)  
706 7996–8003. <https://doi.org/10.1021/jp511846z>.
- 707 [47] A.G. Macdiarmid, J.-C. Chiang, W. Huang, B.D. Humphrey, N.L.D. Somasiri, Polyaniline:  
708 Protonic Acid Doping to the Metallic Regime, *Mol. Cryst. Liq. Cryst.* 125 (1985) 309–318.  
709 <https://doi.org/10.1080/00268948508080110>.
- 710 [48] A. Pandey, Structural And Optical Properties Of Bulk MoS<sub>2</sub> For 2D Layer Growth, *Adv.*  
711 *Mater. Lett.* 7 (2016) 777–782. <https://doi.org/10.5185/amlett.2016.6364>.
- 712 [49] S.H. Patil, A.P. Gaikwad, S.D. Sathaye, K.R. Patil, To form layer by layer composite film in  
713 view of its application as supercapacitor electrode by exploiting the techniques of thin films  
714 formation just around the corner, *Electrochim. Acta.* 265 (2018) 556–568.  
715 <https://doi.org/10.1016/j.electacta.2018.01.165>.
- 716 [50] D. Mombrú, M. Romero, R. Faccio, A.W. Mombrú, Polyaniline intercalated with MoS<sub>2</sub>  
717 nanosheets: structural, electric and thermoelectric properties, *J. Mater. Sci. Mater. Electron.*  
718 29 (2018) 17445–17453. <https://doi.org/10.1007/s10854-018-9844-z>.
- 719 [51] W. Wang, F. Yang, C. Chen, L. Zhang, Y. Qin, M. Knez, Tuning the Conductivity of  
720 Polyaniline through Doping by Means of Single Precursor Vapor Phase Infiltration, *Adv.*  
721 *Mater. Interfaces.* 4 (2017) 1600806. <https://doi.org/10.1002/admi.201600806>.
- 722 [52] A. Molina-Sánchez, L. Wirtz, Phonons in single-layer and few-layer MoS<sub>2</sub> and WS<sub>2</sub>, *Phys.*  
723 *Rev. B.* 84 (2011) 155413. <https://doi.org/10.1103/PhysRevB.84.155413>.
- 724 [53] Y. Cao, Y. Lin, J. Wu, X. Huang, Z. Pei, J. Zhou, G. Wang, Two-Dimensional MoS<sub>2</sub> for  
725 Li–S Batteries: Structural Design and Electronic Modulation, *ChemSusChem.* 13 (2020)  
726 1392–1408. <https://doi.org/10.1002/cssc.201902688>.
- 727 [54] S. Santhosh, A.A. Madhavan, A review on the structure, properties and characterization of  
728 2D Molybdenum Disulfide, in: 2019 Adv. Sci. Eng. Technol. Int. Conf., IEEE, 2019: pp. 1–  
729 5. <https://doi.org/10.1109/ICASET.2019.8714360>.
- 730 [55] A. Gupta, A. Bhargav, A. Manthiram, Highly Solvating Electrolytes for Lithium–Sulfur

- Batteries, *Adv. Energy Mater.* 9 (2019) 1803096. <https://doi.org/10.1002/aenm.201803096>.
- [56] Q. He, A.T.S. Freiberg, M.U.M. Patel, S. Qian, H.A. Gasteiger, Operando Identification of Liquid Intermediates in Lithium–Sulfur Batteries via Transmission UV–vis Spectroscopy, *J. Electrochem. Soc.* 167 (2020) 080508. <https://doi.org/10.1149/1945-7111/ab8645>.
- [57] A. Kawase, S. Shirai, Y. Yamoto, R. Arakawa, T. Takata, Electrochemical reactions of lithium–sulfur batteries: an analytical study using the organic conversion technique, *Phys. Chem. Chem. Phys.* 16 (2014) 9344–9350. <https://doi.org/10.1039/C4CP00958D>.
- [58] J. Zheng, X. Fan, G. Ji, H. Wang, S. Hou, K.C. DeMella, S.R. Raghavan, J. Wang, K. Xu, C. Wang, Manipulating electrolyte and solid electrolyte interphase to enable safe and efficient Li-S batteries, *Nano Energy*. 50 (2018) 431–440. <https://doi.org/10.1016/j.nanoen.2018.05.065>.
- [59] D. Versaci, M. Cozzarin, J. Amici, C. Francia, E.P.M. Leiva, A. Visintin, S. Bodoardo, Influence of synthesis parameters on g-C<sub>3</sub>N<sub>4</sub> polysulfides trapping: A systematic study, *Appl. Mater. Today*. 25 (2021) 101169. <https://doi.org/10.1016/j.apmt.2021.101169>.
- [60] J. Wu, X. Li, H. Zeng, Y. Xue, F. Chen, Z. Xue, Y. Ye, X. Xie, Fast electrochemical kinetics and strong polysulfide adsorption by a highly oriented MoS<sub>2</sub> nanosheet@N-doped carbon interlayer for lithium-sulfur batteries, *J. Mater. Chem. A*. 7 (2019) 7897–7906. <https://doi.org/10.1039/c9ta00458k>.
- [61] S. Evers, L.F. Nazar, New approaches for high energy density lithium-sulfur battery cathodes, *Acc. Chem. Res.* 46 (2013) 1135–1143. <https://doi.org/10.1021/ar3001348>.
- [62] R. Xu, J. Lu, K. Amine, Progress in Mechanistic Understanding and Characterization Techniques of Li-S Batteries, *Adv. Energy Mater.* 5 (2015) 1–22. <https://doi.org/10.1002/aenm.201500408>.
- [63] X. Huang, Z. Wang, R. Knibbe, B. Luo, S.A. Ahad, D. Sun, L. Wang, Cyclic Voltammetry in Lithium–Sulfur Batteries—Challenges and Opportunities, *Energy Technol.* 7 (2019) 1–13. <https://doi.org/10.1002/ente.201801001>.
- [64] X. Li, M. Rao, H. Lin, D. Chen, Y. Liu, S. Liu, Y. Liao, L. Xing, M. Xu, W. Li, Sulfur loaded in curved graphene and coated with conductive polyaniline: preparation and performance as a cathode for lithium–sulfur batteries, *J. Mater. Chem. A*. 3 (2015) 18098–

18104. <https://doi.org/10.1039/C5TA02207J>.
- [65] W. Yang, W. Yang, L. Dong, X. Gao, G. Wang, G. Shao, Enabling immobilization and conversion of polysulfides through a nitrogen-doped carbon nanotubes/ultrathin MoS<sub>2</sub> nanosheet core-shell architecture for lithium-sulfur batteries, *J. Mater. Chem. A*. 7 (2019) 13103–13112. <https://doi.org/10.1039/C9TA03227D>.
- [66] L. Yan, N. Luo, W. Kong, S. Luo, H. Wu, K. Jiang, Q. Li, S. Fan, W. Duan, J. Wang, Enhanced performance of lithium-sulfur batteries with an ultrathin and lightweight MoS<sub>2</sub>/carbon nanotube interlayer, *J. Power Sources*. 389 (2018) 169–177. <https://doi.org/10.1016/j.jpowsour.2018.04.015>.
- [67] W. Yang, W. Yang, L. Dong, X. Gao, G. Wang, G. Shao, Enabling immobilization and conversion of polysulfides through a nitrogen-doped carbon nanotubes/ultrathin MoS<sub>2</sub> nanosheet core-shell architecture for lithium-sulfur batteries, *J. Mater. Chem. A*. 7 (2019) 13103–13112. <https://doi.org/10.1039/c9ta03227d>.
- [68] Y. Wei, Z. Kong, Y. Pan, Y. Cao, D. Long, J. Wang, W. Qiao, L. Ling, Sulfur film sandwiched between few-layered MoS<sub>2</sub> electrocatalysts and conductive reduced graphene oxide as a robust cathode for advanced lithium-sulfur batteries, *J. Mater. Chem. A*. 6 (2018) 5899–5909. <https://doi.org/10.1039/c8ta00222c>.
- [69] J. Ren, Y. Zhou, L. Xia, Q. Zheng, J. Liao, E. Long, F. Xie, C. Xu, D. Lin, Rational design of a multidimensional N-doped porous carbon/MoS<sub>2</sub>/CNT nano-architecture hybrid for high performance lithium-sulfur batteries, *J. Mater. Chem. A*. 6 (2018) 13835–13847. <https://doi.org/10.1039/C8TA04675A>.
- [70] F. Sun, H. Tang, B. Zhang, X. Li, C. Yin, Z. Yue, L. Zhou, Y. Li, J. Shi, PEO-Linked MoS<sub>2</sub>-Graphene Nanocomposites with 2D Polar-Nonpolar Amphoteric Surfaces as Sulfur Hosts for High-Performance Li-S Batteries, *ACS Sustain. Chem. Eng.* 6 (2018) 974–982. <https://doi.org/10.1021/acssuschemeng.7b03306>.
- [71] L. Xiao, Y. Cao, J. Xiao, B. Schwenzer, M.H. Engelhard, L. V. Saraf, Z. Nie, G.J. Exarhos, J. Liu, A Soft Approach to Encapsulate Sulfur: Polyaniline Nanotubes for Lithium-Sulfur Batteries with Long Cycle Life, *Adv. Mater.* 24 (2012) 1176–1181. <https://doi.org/10.1002/adma.201103392>.

- 789 [72] K. Ding, Y. Bu, Q. Liu, T. Li, K. Meng, Y. Wang, Ternary-layered nitrogen-doped  
790 graphene/sulfur/ polyaniline nanoarchitecture for the high-performance of lithium–sulfur  
791 batteries, *J. Mater. Chem. A*. 3 (2015) 8022–8027. <https://doi.org/10.1039/C5TA01195G>.
- 792 [73] D. Wang, X. Hong, S. Liu, X. Ge, B. Tang, H. Wang, K. Xie, W. Ren, Reversible  
793 insertion/extraction of polysulfides into/from polyaniline as an effective strategy to confine  
794 polysulfides in lithium-sulfur batteries, *Ionics* (Kiel). 26 (2020) 191–199.  
795 <https://doi.org/10.1007/s11581-019-03209-9>.

796

797