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Original

Molybdenum disulfide/polyaniline interlayer for lithium polysulphide trapping in lithium-sulphur batteries / Versaci, D.; Canale, I.; Goswami, S.; Amici, J.; Francia, C.; Fortunato, E.; Martins, R.; Pereira, L.; Bodoardo, S.. - In: JOURNAL OF POWER SOURCES. - ISSN 0378-7753. - ELETTRONICO. - 521:(2022), p. 230945. [10.1016/j.jpowsour.2021.230945]

Availability:

This version is available at: 11583/2949679 since: 2022-01-13T14:11:19Z

Publisher:

Elsevier B.V.

Published

DOI:10.1016/j.jpowsour.2021.230945

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<http://dx.doi.org/10.1016/j.jpowsour.2021.230945>

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

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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⁻¹,
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, MoS₂ 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 MoS₂, 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 MoS₂/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⁻¹, 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⁻¹ [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 S₈ ring is reduced, forming high order lithium polysulfides (LiPSs, Li₂S_x (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 Li₂S [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 Li_2S_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 (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 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 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, MoS₂ 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, MoS₂ 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 MoS₂ with
92 sulphur-free locations [28] and the stronger interaction between the edge sites of MoS₂ and LiPSs
93 than those of basal surface sites [25]. Last but not least, the different phase structures of MoS₂
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 MoS₂ in an aqueous media. PANI and
136 MoS₂ 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 H₂SO₄ (0.5 M, Sigma Aldrich, purity 95 – 97%) was prepared and then chemically treated with
141 PSA ((NH₄)₂S₂O₈, 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 MoS₂ (hexagonal molybdenum (IV) sulfide, powder, $<$ 2 μ m,
147 99%).

148 As few MoS₂ layers have significantly better properties than the bulk form, an exfoliation process
149 was carried out on commercial bulk MoS₂. Typically, the exfoliation of commercial MoS₂ requires
150 a "solvent-assisted" process in which solvents with surface tension as close as possible to the
151 surface energy of MoS₂ are adopted. In our case, MoS₂ 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 MoS₂ and PANI were: 100:0,
154 0:100, 30:70 and 70:30 wt%, respectively named: MoS₂, PANI, MoS₂:PANI 3:7 and MoS₂: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° 2θ with a step size of 0.026 2θ
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⁻¹ from 4000 to 400 cm⁻¹.

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 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 MoS_2 , PANI or a mixture of them. The ratio between 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 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, H_2O and 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 μm 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 ($\text{CF}_3\text{SO}_2\text{N}(\text{LiSO}_2\text{CF}_3)_2$, LiTFSI) and 0.25 M lithium nitrate
199 (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 μL ,
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. Li^+/Li^0 at different
205 current rates. The C-rate was calculated using the theoretical capacity of sulphur (1672 mAh 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. Li^+/Li^0 at 0.1 mV s^{-1} .

208 The catalytic effect of MoS_2 and PANI on polysulfide redox conversion reaction was elucidated
209 by exchange current density obtained from LSV analysis with a Li_2S_6 catholyte solution. In this
210 case, the working electrode containing 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 Li_2S_6 solution directly prepared
213 in LiTFSI (1 M) in DME:DIOX 1:1 v/v + 0.25 M LiNO_3 electrolyte, mixing Li_2S and 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 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 MoS₂/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 MoS₂ 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 MoS₂/PANI composites are shown in Figure 2. The morphology of commercial untreated MoS₂, shows adhered and stacked sheets, by van der Waals forces. In figure 2b a wide number of stacked and compressed MoS₂ 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, MoS₂:PANI 3:7 shows highly compact structure with dimension and shape similar to the ones observed for pure PANI. Moreover, some well exfoliated MoS₂ nanosheets can be clearly identified (Figure e and f). The morphology of MoS₂:PANI 7:3 composite appears less

compact, and the presence of the individual MoS₂ sheets is predominant as expected (Figure g and h).

Please insert here Figure 2.

X-ray-diffraction (XRD) patterns of as-prepared MoS₂/PANI composites are shown in Figure 3a. The XRD pattern of bare bulk MoS₂ well matches with JCPDS (77-1716) of polycrystalline MoS₂. The bare MoS₂ 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 MoS₂ samples, but in the XRD pattern of MoS₂: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⁻¹ 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⁻¹. 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⁺ stretching mode) as consequence of PANI protonation and/or oxidation after acid or complexation treatment. The intense peak observed at 1610 cm⁻¹ is assigned to C=C stretching vibrations mode in quinoid ring. The shift of this peak, generally observable at 1592 cm⁻¹, is attributable to the doped nature of

263 polyaniline [51]. Less pronounced peaks at 1491, 1418 and 1219 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 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 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 cm^{-1} which could be associated to MoS_2 , in addition to the typical
272 peaks linked to the emeraldine form of PANI. Concerning the composite containing higher amount
273 of 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 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 cm^{-1} the C-N stretching modes of aromatic amine group are
279 observable, while the peak at 1196 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 MoS_2 /PANI composites.

282

283 *Please insert here Figure 3.*

284

285 To evaluate the LiPSs adsorption capability 20 μ L of 1.0 mM of Li_2S_6 solution diluted in 2 mL of
286 DME:DIOX 1:1 v/v mixture were respectively added to 50 mg of MoS_2 , PANI, MoS_2 :PANI 3:7
287 and 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 Li_2S_6 (Figure SI1a).

289 In order to confirm the interaction between 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 Li_2S_4 , Li_2S_6 and Li_2S_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 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 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 Li_2S_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-MoS₂ and DL-
310 MoS₂: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-MoS₂
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-MoS₂:PANI 3:7 and
314 DL-MoS₂: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 MoS₂. 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 5th 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 MoS₂ 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 1st and 2nd 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 α -S₈ ring opening and the consequent formation and reduction of long chain lithium polysulfides (Li₂S_x, 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 (Li₂S_x, 1 < x < 4) and consequently to final Li₂S. It is worth noting that, during the different processes, disproportionation reactions occur resulting in the simultaneous coexistence of multiple species [61], even if Li₂S₆ and Li₂S₄ 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 MoS₂, 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 MoS₂.

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 1st 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-MoS₂, DL-MoS₂:PANI 3:7 and DL-MoS₂:PANI 7:3, respectively. At the same time,
361 the 2nd 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 MoS₂:PANI 3:7 show a shoulder at around 2.63 V, while DL with pure MoS₂ and MoS₂: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 (MoS₂ 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.** 1st and 2nd order derivative for the first anodic and cathodic branch of cyclic
 379 voltammetry, for all the samples.

380

		SL	DL-PANI	DL-MOS ₂	DL- MOS ₂ :PANI 3:7	DL- MOS ₂ :PANI 7:3
<i>Cycle 1</i>		<i>Cathodic</i>				
δI/δE (A V⁻¹)	Peak 1	2.20	2.20	2.22	2.20	2.22
	Peak 2	1.95	1.92	1.97	1.89	1.88
δ²I/δE² (A V⁻²)	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>				
δI/δE (A V⁻¹)	Peak 1	2.44	2.58	2.50	2.52	2.52

$\delta^2 I / \delta E^2$ (A V ⁻²)	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 MoS₂ 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 MoS₂ 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 MoS₂ 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⁻¹. DL cathodes containing
394 pure MoS₂, pure PANI, MoS₂:PANI 3:7 and MoS₂:PANI 7:3 deliver 1100, 1450, 1180, and 1240
395 mAh g⁻¹ 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⁻¹ 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⁻¹ 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 MoS₂ coating. DL containing pure PANI shows a specific capacity of 355 mAh g⁻¹, DL with pure MoS₂ shows a higher specific capacity of about 480 mAh g⁻¹, while the two DLs containing a mixture of MoS₂ and PANI show a specific capacity close to 600 mAh g⁻¹ 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 MoS₂ [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, MoS₂, MoS₂:PANI 3:7 and MoS₂: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, MoS₂, MoS₂:PANI 3:7 and MoS₂: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 MoS₂.

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 MoS₂ 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 MoS₂ 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 5th cycle (C/5), SL cathode
428 shows higher ΔE value (265 mV), followed by DL-PANI (264 mV), DL-MoS₂:PANI 3:7 (251 mV),
429 DL-MoS₂:PANI 7:3 (219 mV) and DL-MoS₂ (216 mV). The voltage hysteresis trend of DL
430 electrodes, especially at higher C-rates, points out the active role of MoS₂ 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 LiS₂ final
441 product. On the contrary, the contribution of MoS₂ 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 500th 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 Li₂S 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 MoS₂. 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 MoS₂ and PANI, or their combination, improves the
462 efficiency of the conversion reaction of polysulfides to Li₂S, for more than 500 cycles. It is
463 important to note that the lower Q2/Q1 value, obtained for SL at 500th 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 MoS₂ 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 MoS₂ 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 x 10⁻⁴, 3.8/3.7 x 10⁻¹ and 1.8/2.7 x 10⁻³ mA cm⁻² for KJB, MoS₂ and PANI, respectively.
471 These values prove the accelerated conversion of LiPS due to the presence of MoS₂, a lower
472 catalytic effect of PANI and the inconspicuous role of KJB.

473 These results confirm that MoS₂ 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 MoS₂ can spatially regulate the deposition of
476 Li₂S, 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 MoS₂ (Figure 6e,f) appears smoother with few cracks, meaning that the
492 presence of MoS₂ 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 MoS₂: 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 MoS₂ (Figure 6i,j) shows a smooth and
496 compact structure. In both samples MoS₂ 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 MoS₂ 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.*

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4. CONCLUSIONS

In summary, we investigated the ability of MoS₂ 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, MoS₂ 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 MoS₂ 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 MoS₂ induces a catalytic effect on the LiPSs conversion reaction, improving the electrochemical performances of the cathode.

In particular, the implementation of DL-MoS₂:PANI 7:3 noticeably improved the electrochemical behaviour of the sulphur cathode, showing a final specific capacity close to 600 mAh g⁻¹, 42 % higher than the standard sulphur cathode, after 500 cycles.

Therefore, the use of MoS₂/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 MoS₂/PANI assembly (b).

546 **Fig. 2.** FESEM micrographs of: bare MoS₂ (a,b), bare PANI (c,d), MoS₂:PANI 3:7 (e,f) and
547 MoS₂:PANI 7:3 (g,h).

548 **Fig. 3.** XRD spectra of bare MoS₂, bare PANI, MoS₂:PANI 3:7, and MoS₂: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⁻¹, 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 5th charge–discharge curves at C/5 (d), Q1% comparison
556 (e) and Q1/Q2 ratio (f) for different cycles, Tafel plots of the Li₂S₆ solution redox on PANI or
557 MoS₂ 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 MoS₂ (e,f), DL-MoS₂:PANI 3:7 (g,h) and DL-MoS₂:PANI 7:3 (i,j).

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

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562

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