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

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ABSTRACT

Lithium-sulphur battery technology promises much higher energy storage capacity compared to common Li-ion commercial batteries. Li-S batteries have high theoretical capacity of 1672 mAh g^{-1}, thanks to conversion reaction from solid sulphur to lithium polysulfides (LiPSs). Unfortunately, few issues are still hindering their commercialization. The main problem afflicting lithium sulphur batteries is the shuttle phenomenon, due to soluble long chain LiPSs generated at the cathode. In the last years, many interlayer separators have been based on materials showing physical blocking of LiPSs. In particular, MoS_2 and PANI separately showed strong adsorption capability, preventing polysulfides dissolution and accelerating the redox reaction kinetics. In the present work we rationally design, for the first time, composite materials based on PANI and MoS_2, with the aim to evaluate the specific role of each component and their synergy as LiPSs blocking-agents, by implementation of a second layer containing the MoS_2/PANI composite directly on the top of the standard S/C electrode. The systematic study confirms that double-layer containing the composite remarkably improves the performance of the sulphur cathode, showing specific capacity close to 600 mAh g^{-1}, which is 42 % higher than the standard sulphur cathode, after 500 cycles.

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 S_8 ring is reduced, forming high order lithium polysulfides (LiPSs, Li_2S_x ($4 > x \leq 8$)), 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_2S [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 though 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

system. In addition, MoS_2 promotes the redox reaction kinetics of LiPSs (from long-chain to short-chain polysulfides) during the discharge/charge processes, acting as a lithium ion conductor. This way, the fast conversion of the soluble polysulfides decreases their accumulation into the electrolyte and inhibits their subsequent loss from the electrode [19][25][27]. In general, MoS_2 layers provide a large active conductive surface area ideal for a successful PS trapping, with great flexibility. However, both the absorption of the polysulphides and the catalytic activity strongly depend on chemical composition, surface functionality and intrinsic electronic structure of the catalyst [19][26][27]. Typically, the redox reactions occur through strong polysulfides adsorption, rapid interfacial charge transfer and product deposition. This means that the variation of surface adsorption behaviour can tune the activation energies of chemical reactions and promote the redox reaction kinetics [19]. These are at the basis of the higher electrochemical activity of MoS_2 with sulphur-free locations [28] and the stronger interaction between the edge sites of MoS_2 and LiPSs than those of basal surface sites [25]. Last but not least, the different phase structures of MoS_2 (hexagonal and tetragonal symmetry) have different catalytic behaviours as a consequence of different electronic properties [18][26][27].

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

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

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

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

Unlike previous reports, which separately investigate the role of PANI and MoS_2, in this work we study PANI/MoS_2 composites, with the purpose of evaluating the different role of each component as LiPSs blocking agents. To date, a systematic study, properly comparing the role PANI/MoS_2 composites as LiPSs blocking agent and the different behavior of the two components is lacking. In addition, most published studies are difficult to compare, because of different test parameters, such 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_2 in an aqueous media. PANI and
136 MoS_2 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 ≥ 99.5 %)-and
140 H_2SO_4 (0.5 M, Sigma Aldrich, purity 95 – 97%) was prepared and then chemically treated with
141 PSA ($(NH_4)_2S_2O_8$, 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_2 (hexagonal molybdenum (IV) sulfide, powder, < 2μm,
147 99%).

148 As few MoS_2 layers have significantly better properties than the bulk form, an exfoliation process
149 was carried out on commercial bulk MoS_2. Typically, the exfoliation of commercial MoS_2 requires
150 a "solvent-assisted" process in which solvents with surface tension as close as possible to the
151 surface energy of MoS_2 are adopted. In our case, MoS_2 powder was placed in a beaker containing

water and PANI and was subjected to ultra-sonication process for 9 hours at 300 W, avoiding the use of other solvents or additives. The selected ratio adopted between MoS_2 and PANI were: 100:0, 0:100, 30:70 and 70:30 wt%, respectively named: MoS_2, PANI, MoS_2:PANI 3:7 and MoS_2:PANI 7:3. This choice was made in order to discriminate the contribution and the role of the two components on the final electrochemical performances.

2.2. Material characterization

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

Fourier Transform Infrared Spectroscopy (FTIR) was measured with a Nicolet™ iS50 FTIR spectrometer (Thermo Scientific™) equipped with ATR tool. 32 scans were collected with a resolution of 4 cm^{-1} from 4000 to 400 cm^{-1}.

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

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

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

2.3. Electrochemical measurements

All working electrodes were prepared by solvent tape casting method. The so called "standard" sulphur cathode electrode (SL) was prepared using pure sulphur (Sigma Aldrich ≥ 99.5 %) as active material, Ketjenblack® (KjB, EC-300J, AkzoNobel), as conductive carbon additive and poly(vinylidenedifluoride) (PVdF, Kynar 761, Arkema; 10 wt.% in N-methyl-2-pyrrolidinone solution) as polymeric binder. The standard single-layer electrode composition was set up to 70:30:10 wt%, respectively for S:KjB:PVdF, in all experiments. Ketjenblack® carbon was selected because is an inexpensive and highly conductive carbon, with high specific surface area and high pore volume, which are optimal properties to confine sulphur [46]. The S/KjB mixture (SL) was mechanically deposited on the aluminium current collector by an automatic film applicator (Sheen 1133N) with a speed of 50 mm s^{-1}, adjusting the Doctor Blade thickness at 200 µm. The wet electrode was dried in an oven at 50 °C in air. A similar procedure was used to obtain double layer (DL) cathodes. The dried single-layer electrode was subsequently coated by a second layer containing MoS_2, PANI or a mixture of them. The ratio between MoS_2 and/or PANI, KjB and PVDF, was 80:10:10, with a blade thickness of 200 µm.

After solvent evaporation in air, disks of 1.76 cm^2 were punched out, vacuum dried at 40 °C (in a Büchi Glass Oven B-585) for 4 h, then transferred into an Argon filled dry glove-box (MBraum Labstar, H_2O and O_2 content < 1 ppm) for cell assembly. The active material loading of the "standard" sulphur cathode was ~ 1 – 1.2 mg cm^{-2}.

The electrochemical characterization was carried out in CR2032 coin cells, with lithium disk (Chemetall Foote Corporation, Ø 16 mm) as counter electrode and PP polymeric membrane

196 (Celgard 2500, 25 μm thickness, Ø 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 ($CF_3SO_2NLiSO_2CF_3$, LiTFSI) and 0.25 M lithium nitrate
199 ($LiNO_3$, ≥ 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 ~ 10 - 11 μL 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 MoS_2/PANI

PANI was synthetized 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_2 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_2/PANI composites are shown in Figure 2. The morphology of commercial untreated MoS_2, shows adhered and stacked sheets, by van der Waals forces. In figure 2b a wide number of stacked and compressed MoS_2 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_2:PANI 3:7 shows highly compact structure with dimension and shape similar to the ones observed for pure PANI. Moreover, some well exfoliated MoS_2 nanosheets can be clearly identified (Figure e and f). The morphology of MoS_2:PANI 7:3 composite appears less

compact, and the presence of the individual MoS_2 sheets is predominant as expected (Figure g and h).

Please insert here Figure 2.

X-ray-diffraction (XRD) patterns of as-prepared MoS_2/PANI composites are shown in Figure 3a. The XRD pattern of bare bulk MoS_2 well matches with JCPDS (77-1716) of polycrystalline MoS_2. The bare MoS_2 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_2 samples, but in the XRD pattern of MoS_2: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 ($C\text{-}N^{+\cdot}$ 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

polyaniline [51]. Less pronounced peaks at 1491, 1418 and 1219 cm^{-1}, are ascribable to the C=N, C=C stretching of the quinoid units, and C-N stretching of benzenoid units, respectively [29][50][51]. The Raman spectrum of commercial MoS_2 powders confirms that the material is in bulk form. The E^1_{2g} peak, located at 383.4, is due to in-plane vibration modes of the S atoms, while A_{1g} peak located at 407.5 cm^{-1} is due to out-off-plane vibration modes of S atoms. The peaks position is layer dependent, and varies according to the number of stacked layers. Typically, E^1_{2g} moves towards lower frequencies while A_{1g} shows a shift towards higher frequencies as the number of layers increases [52][53][54]. In the composite containing higher amounts of PANI, it is possible to notice a signal at about 400 cm^{-1} which could be associated to MoS_2, in addition to the typical peaks linked to the emeraldine form of PANI. Concerning the composite containing higher amount of MoS_2, the two peaks ascribable to molybdenum disulphide can be prevalently seen, while the typical signals of emeraldine form are observed at higher wavelength [50].

The samples were also characterized by FTIR/ATR spectroscopy (Figure 3c and d). In the samples containing PANI, the adsorption bands at 1626 and 1521 cm^{-1} are assigned to N-H bending of amine and C=C stretching vibrations of the quinonoid and benzenoid ring, respectively. In the region between 1200 and 1400 cm^{-1} the C-N stretching modes of aromatic amine group are observable, while the peak at 1196 cm^{-1} is ascribable to the vibrational mode band of $Q=N^+H=B$ or B–NH–B, typical for PANI doped structure [16]. These results clearly indicate the presence of PANI in its doped emeraldine state in all the MoS_2/PANI composites.

Please insert here Figure 3.

To evaluate the LiPSs adsorption capability 20 μL of 1.0 mM of Li_2S_6 solution diluted in 2 mL of DME:DIOX 1:1 v/v mixture were respectively added to 50 mg of MoS_2, PANI, MoS_2:PANI 3:7 and MoS_2:PANI 7:3 (Figure SI1). After resting the samples for 12 hours, all the solutions showed colour fading, demonstrating an interaction with Li_2S_6 (Figure SI1a).

In order to confirm the interaction between MoS_2, PANI and their combination with LiPSs, an UV-Vis absorption experiment was performed (Figure SI1b). Observing the UV-Vis spectra comparison, in the range between 350 – 500 nm, the solution containing the synthetized materials shows a remarkable absorption intensity decrease, which is consistent with the colour fading observed in the solutions after 12 h. In fact Li_2S_4, Li_2S_6 and Li_2S_8 species produce characteristic peaks in the region above 300 nm, respectively at 400, 430, and around 500 nm [55][56][57], while elemental sulphur exhibits strong absorption below 300 nm [58][59]. These suggests the effective and enhanced LiPSs entrapment capability of MoS_2 and PANI based materials.

3.3. Electrochemical characterization

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

Single-layer and double layer electrodes exhibit the characteristic reduction/oxidation peaks of S. More in detail, the cathodic scans exhibit two pronounced peaks corresponding to the reduction of elemental sulphur (α-S_8) to long chain lithium polysulfides Li_2S_x ($4 < x < 8$) and the consequent reduction of long-chain polysulfides to solid Li_2S_2/Li_2S.

A comparison of the voltammograms points out that the first reduction peak shape is similar for all the samples. The reaction starts at 2.39 V for all cathodes, except the DL-PANI one, for which the reaction starts at higher voltage (2.45 V). Concerning the peak position, SL and DL electrodes are superimposed at around 2.20 V, small shifts at 2.22V are seen for DL-MoS_2 and DL-MoS_2:PANI 7:3. The second reduction starts at the same potential (2.07 V) for all the samples. DL-PANI shows similar shape to SL cathode but higher intensity, while the peak position of DL-MoS_2 is slightly shifted at higher potential (1.97 V) and less pronounced. Similarly, for the mixed DL, the peaks appear broader and shifted at lower potential (1.89 and 1.88 V for DL-MoS_2:PANI 3:7 and DL-MoS2:PANI 7:3, respectively). An interesting aspect is that the curve profile of the two composites seem to be deriving from the combination of the profiles of DL electrodes containing either pure PANI or pure MoS_2. This behaviour can be deducible observing the intermediate intensity of the peaks and the clear presence of shoulders in the DL composites profiles.

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

At the 5^{th} cycle (Figure 4b), CV profiles show slight shifts. Particularly, the first reduction peak of the SL standard cathode shows a shift at higher voltages, while the DL cathodes containing PANI show a shift for the second reduction peak. On the contrary DL cathode containing pure MoS_2 does not show any evident peak shift.

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

329

330 *Please insert here Figure 4.*

331

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

335 Observing the voltammograms of all the cathodes, both cathodic peaks show at least two
336 shoulders (Figure SI2a). In particular, the first cathodic peak shows one shoulder at higher potential
337 (range: 2.25 – 2.31 V) and a second shoulder at lower potential (range: 2.16 – 2.19 V). At the same
338 time, the second cathodic peak presents two shoulders, in the ranges of 2.01 – 2.03 and 1.87 – 1.94
339 V, respectively. It is important to note that the two mixed DL electrodes show additional shoulders
340 in the range of 1.76 – 1.80 V. As widely reported, the presence of different peaks/shoulders are
341 assigned to the different reduction reactions of the discharge (Figure SI2b). In particular, the
342 process at higher voltages can be related to α-S_8 ring opening and the consequent formation and
343 reduction of long chain lithium polysulfides (Li_2S_x, $4 < x < 8$). While the second reduction peak and
344 the related shoulders are attributable to soluble high order LiPSs that are converted to short chain
345 lithium polysulfides (Li_2S_x, $1 < x < 4$) and consequently to final Li_2S. It is worth noting that, during
346 the different processes, disproportionation reactions occur resulting in the simultaneous coexistence
347 of multiple species [61], even if Li_2S_6 and Li_2S_4 are generally reported as the most stable
348 intermediate polysulfides [62]. The presence of evident and well-defined shoulders for the DL
349 electrodes containing both PANI and MoS_2, suggests that the concomitant presence of these
350 materials shift and emphasises some reactions. This typical behaviour can be due to the physico-
351 chemical interaction of lithium polysulfides with PANI and/or MoS_2.

In the subsequent anodic scan, only one broad oxidation peak, located in the potential range of 2.2 – 2.6 V, is clearly seen. Comparing the CVs, the oxidation reaction of all DL electrodes starts at lower potential, at around 2.16 V instead of 2.25 V (observed for SL electrode). Concerning the peaks shape and position, DL electrodes show visible shifts at higher voltages, as a consequence of broader profiles. A broader profile indicates the presence of numerous species, which undergo oxidation, over a wide range of potentials. In this case also, the 1st order derivative allows to identify the correct peaks position (Figure SI3a). The SL electrode shows a peak at lower potential (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 DL-PANI, DL-MoS_2, DL-MoS_2:PANI 3:7 and DL-MoS_2:PANI 7:3, respectively. At the same time, the 2nd order derivative curve allows to identify the inflection points of the voltammograms, located in correspondence to the peak shoulders (Figure SI3b). The SL electrode shows two shoulders at lower (2.37 V) and higher (2.55 V) voltages than the main peak. The same inflection points were found for the DL electrodes, but slightly shifted, as reported in Table 1. Two additional inflection points are reported for DL electrodes. In particular, the DL electrodes containing pure PANI and MoS_2:PANI 3:7 show a shoulder at around 2.63 V, while DL with pure MoS_2 and MoS_2:PANI 7:3 show a shoulder at lower voltage, around 2.44 V. These processes, occurring in the range of 2.45 – 2.64 V, are typical of the oxidation reaction of medium-chain polysulfides to long chain polysulfides. While the reaction occurring at lower voltages (2.37 V) is related to short chain polysulfides conversion to medium chain polysulfides species.

Generally, the broader shape observed for the DL electrodes is due to the presence of the second layer and to the consequent smaller ion diffusion typical of thicker electrodes [63]. But in this case the different peak shape can be strictly related to the different amount of each single component (MoS_2 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
Cycle 1				***Cathodic***		
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
$\delta^2I/\delta E^2$ (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
Cycle 1				***Anodic***		
δI/δE (A V^{-1})	Peak 1	2.44	2.58	2.50	2.52	2.52

$\delta^2I/\delta E^2$ ($A\ V^{-2}$)	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 MoS_2 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_2 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_2 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 MoS_2, pure PANI, MoS_2:PANI 3:7 and MoS_2: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 MoS_2 coating. DL containing pure PANI shows a specific capacity of 355 mAh g^{-1}, DL with pure MoS_2 shows a higher specific capacity of about 480 mAh g^{-1}, while the two DLs containing a mixture of MoS_2 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 MoS_2 [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_2, MoS_2:PANI 3:7 and MoS_2: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_2, MoS_2:PANI 3:7 and MoS_2: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_2.

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_2 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

was already observed in previous work adopting MoS_2 in lithium sulphur systems [44]. Nevertheless, the charge curve profile is similar for all the samples, showing only the two typical oxidation reaction plateaus.

The voltage hysteresis between charge and discharge curves confirms a higher overpotential for the SL electrode (Figure 5c). Analysing the voltage hysteresis for the 5^{th} cycle (C/5), SL cathode shows higher ΔE value (265 mV), followed by DL-PANI (264 mV), DL-MoS_2:PANI 3:7 (251 mV), DL-MoS_2:PANI 7:3 (219 mV) and DL-MoS_2 (216 mV). The voltage hysteresis trend of DL electrodes, especially at higher C-rates, points out the active role of MoS_2 in promoting polysulfides conversion reaction.

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

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

The dQ/dV vs V profiles at higher cycle number at C/5 (Figure SI6b) it is important to note that the presence of PANI in the double layer induces a higher contribution to the lower voltage reduction reaction due to the reversible conversion reaction of short-chain polysulfides to LiS_2 final product. On the contrary, the contribution of MoS_2 seems more pronounced to higher voltage reduction reaction, which involves the long-chain polysulfides conversion to short-chain species. The trend is confirmed in the anodic branch, but increasing the number of cycles a balancing of the 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^{th} 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_2S 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_2. 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_2 and PANI, or their combination, improves the
462 efficiency of the conversion reaction of polysulfides to Li_2S, for more than 500 cycles. It is
463 important to note that the lower Q2/Q1 value, obtained for SL at 500^{th} 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_2 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_2 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, MoS_2 and PANI, respectively.
471 These values prove the accelerated conversion of LiPS due to the presence of MoS_2, a lower
472 catalytic effect of PANI and the inconspicuous role of KjB.

473 These results confirm that MoS_2 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_2 can spatially regulate the deposition of
476 Li_2S, 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

electrode with pure MoS_2 (Figure 6e,f) appears smoother with few cracks, meaning that the presence of MoS_2 helps to achieve a more compact structure of the double-layer. The same consideration can be done comparing the DL electrodes with a mixture of PANI and MoS_2: the sample containing excess of PANI (Figure 6g,h) presents an electrode surface rich of pores and cracks, while the electrode containing a higher amount of MoS_2 (Figure 6i,j) shows a smooth and compact structure. In both samples MoS_2 and PANI are homogeneously distributed on the surface.

Please insert here Figure 6.

In conclusion, the 3D framework originated by the mixing of the two compounds provides fast electrons and ions transport pathways during the electrochemical process. In DL electrodes the combination of MoS_2 and PANI is able to trap polysulfide species inside the top layer, thus alleviating the shuttle effect thanks to the synergic contribution of the two compounds. In addition, the use of a second layer increases the volume available for sulphur and lithium polysulfides accommodation, preserving the electrolyte infiltration and enabling the movement of lithium ions [46] as depicted in Figure 7.

Please insert here Figure 7.

4. CONCLUSIONS

In summary, we investigated the ability of MoS_2 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_2 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_2 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_2 induces a catalytic effect on the LiPSs conversion reaction, improving the electrochemical performances of the cathode.

In particular, the implementation of DL-MoS_2: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 MoS_2/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.

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Captions to Figures

Fig. 1. Polymerization scheme of aniline emeraldine salt chains (a), schematic illustration of the MoS_2/PANI assembly (b).

Fig. 2. FESEM micrographs of: bare MoS_2 (a,b), bare PANI (c,d), MoS_2:PANI 3:7 (e,f) and MoS_2:PANI 7:3 (g,h).

Fig. 3. XRD spectra of bare MoS_2, bare PANI, MoS_2:PANI 3:7, and MoS_2:PANI 7:3 (a from top to bottom), Raman spectra comparison (b), FTIR/ATR spectra comparison (c) and zoomed area of interest (d).

Fig. 4. Cyclic voltammogram comparison (a), and zoomed area (b) of the fist cycle and of the fifth cycle (c) scan rate 0.1 mV s^{-1}, in the range 1.6 – 2.8 V.

Fig. 5. Comparison of the specific capacity vs. cycle number at C/5 (a), comparison of charge/discharge voltage profiles for the first cycle at C/10 (d), and for the fifth cycle at C/5 (c), plot of dQ/dV vs. V reproduced from the 5^{th} charge–discharge curves at C/5 (d), Q1% comparison (e) and Q1/Q2 ratio (f) for different cycles, Tafel plots of the Li_2S_6 solution redox on PANI or MoS2 materials, derived from LSV scans (g).

Fig. 6. FESEM micrographs of different cathodes: SL standard cathode (a,b), DL-PANI (c,d), DL-MoS_2 (e,f), DL-MoS_2:PANI 3:7 (g,h) and DL-MoS_2:PANI 7:3 (i,j).

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

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