

# Diffusional Features of a Lithium-Sulfur Battery Exploiting Highly-Microporous Activated Carbon

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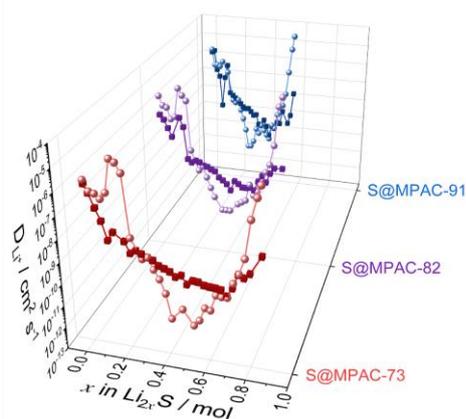
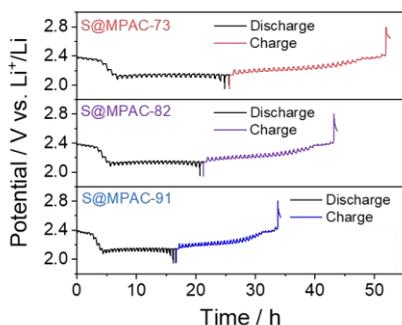
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## Abstract

Diffusion process at the electrode/electrolyte interphase drives the performances of the lithium-sulfur battery, and activated carbon (AC) can remarkably vehicle ions and polysulfide species throughout the two-side liquid/solid region of the interphase. We reveal original findings such as the values of the diffusion coefficient at various states of charge of the Li-S battery using a highly-porous AC, its notable dependence on the adopted techniques, and the correlation of the diffusion trend with the reaction mechanism. X-ray photoelectron spectroscopy (XPS) and X-ray energy dispersive spectroscopy (EDS) identify in the carbon derived from bio-residues heteroatoms such as N, S, O and P which can increase the polarity of the C framework. The transport properties are achieved by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic intermittent titration technique (GITT). The study reveals Li<sup>+</sup>-diffusion coefficient ( $D_{Li^+}$ ) depending on the technique, and values correlated with the cell state of the charge. EIS, CV and GITT show  $D_{Li^+}$  within

$10^{-7}$ – $10^{-8}$   $\text{cm}^2 \text{s}^{-1}$ ,  $10^{-8}$ – $10^{-9}$   $\text{cm}^2 \text{s}^{-1}$ , and  $10^{-6}$ – $10^{-12}$   $\text{cm}^2 \text{s}^{-1}$ , respectively, dropping down at the fully discharged state and rising up upon charge. GITT allows the evaluation of  $D_{\text{Li}^+}$  during the process and evidences the formation of lowly conducting media upon discharge. The sulfur composite delivers in Li-cell a specific capacity ranging from 1300 mAh  $\text{g}^{-1}$  at 0.1C to 700 mAh  $\text{g}^{-1}$  at 2C with S loading of 2  $\text{mg cm}^{-2}$ , and from 1000 to 800 mAh  $\text{g}^{-1}$  at 0.2C when S loading is raised to 6  $\text{mg cm}^{-2}$ .

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**Diffusion process** at the electrode/electrolyte interphase drives the performances of the lithium-sulfur battery, and determines the possible applicability of a cell using activated carbon with enhanced electrochemical conversion process in terms of relevant stability and fast kinetics.

## Introduction

The mitigation of climate change and global warming recently triggered the limitation of greenhouse gas emission, mainly by developing renewable energy source in alternative to fossil fuels and electric vehicles (EVs) instead of combustion-engine cars.<sup>[1]</sup> Meanwhile, the successful management of alternative green energies such as solar and wind, as well as the increase of the EVs driving range and economical sustainability require adequate energy storage systems.<sup>[2]</sup> The current lithium-ion batteries (LIBs) based on intercalation or insertion materials both at the cathode and at the anode side have deeply contributed to the development of the modern consumer electronics and boosted the diffusion of the first generation of EVs.<sup>[3]</sup> In this scenario, many efforts and massive research on alternative batteries characterized by improved energy density, decreased costs and limited

flammability have been undertaken to increase the driving ranges, lower the economic impact, enhance the safety content and trigger the large-scale diffusion of the EVs.<sup>[4,5]</sup> Among the various energy storage systems, lithium-sulfur (Li-S) batteries appeared as the most promising candidate due to a two-electron electrochemical reaction providing high theoretical capacity (1675 mAh g<sup>s-1</sup>) and energy density (2600 Wh kg<sup>s-1</sup>), with practical values exceeding those of the commercial LIBs.<sup>[6,7]</sup> In addition, sulfur holds several bonuses, such as great abundance, low-cost and environmental compatibility.<sup>[8]</sup> Sulfur (S<sub>8</sub>) is insulating at the pristine state, with an electronic conductivity of 5×10<sup>-30</sup> S cm<sup>-1</sup> at 25 °C, whilst its electrochemical reaction in lithium cell involves the formation of both insoluble species such as Li<sub>2</sub>S<sub>2</sub> and Li<sub>2</sub>S that may precipitate in the cell environment, and soluble high-order lithium polysulfides (Li<sub>2</sub>S<sub>x</sub>, 4 ≤ x ≤ 8).<sup>[9]</sup> The above mentioned low conductivity may actually hinder the Li-ion mobility and diffusion, thus lowering the active material utilization and increasing the cell polarization.<sup>[9]</sup> The ions diffusivity in a poorly conductive environment such as the Li-S system has actually a crucial role in driving the cell performances, particularly in terms of overall impedance and rate capability. This aspect has been in part highlighted in various literature reports,<sup>[10,11]</sup> however, its full understanding still needs specific efforts and researches. Instead, the electrochemically active soluble lithium polysulfide intermediates can be directly reduced at the lithium surface to form an irregular solid electrolyte interphase (SEI) layer which increases the cell impedance and gradually decrease the capacity.<sup>[12]</sup> Furthermore, the soluble fraction of the latter reduced species can migrate by diffusion from the anode back to the cathode to be newly oxidized and undergo a *loop reaction* indicated as *shuttle process* leading to a continuous charge without any energy storage, loss of active material, fast capacity fading and poor Coulombic efficiency.<sup>[13-15]</sup> Therefore, the proper design of a suitable electrolyte media was deeply investigated for allowing sufficient safety in view of the use of lithium metal anode, high ionic conductivity and transport number, as well as an adequate SEI at the electrodes, particularly at the Li surface. The most employed electrolyte for Li-S cell consisted of a solution of a lithium salt (e.g., LiTFSI) in dioxolane (DOL) and dimethoxy ethane (DME), which was successfully upgraded by the addition of lithium nitrate

(LiNO<sub>3</sub>) as sacrificial specie which forms at the lithium surface a SEI including carbonates and nitrates that strongly limits the polysulfide shuttle process.<sup>[16]</sup> Furthermore, the replacement of DOL and DME by lowly flammable solvents such as glymes (i.e., ethers with formula CH<sub>3</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>CH<sub>3</sub> and n > 2)<sup>[17]</sup> or polymers (e.g., solid polyethylene glycol, PEG)<sup>[18]</sup> has been indicated as the most suitable pathway to enhance the cell safety. The most explored strategy to mitigate the issues affecting the Li-S cell is to accommodate the sulfur in conductive carbon matrixes, such as graphene and its derivatives,<sup>[19]</sup> carbon nanotubes,<sup>[20]</sup> carbon nanofibers,<sup>[21]</sup> hollow carbon spheres<sup>[22]</sup> or porous carbons.<sup>[23]</sup> Indeed, suitable carbon additives can actually enhance the reaction kinetics and the cell performance by ensuring high electronic and ionic conductivity, large surface area and well-ordered pore system which hold the contact with sulfur and lithium polysulfides by physical absorption *via* weak van der Waals interaction, and accelerate the electron/ion transfer.<sup>[24–</sup>  
<sup>26]</sup> Furthermore, the inclusion of inorganic materials into the above mentioned carbon hosts such as nanometric metals,<sup>[10,11]</sup> metal oxides,<sup>[27]</sup> conductive polymers,<sup>[28]</sup> MOFs,<sup>[29]</sup> or doping heteroatoms<sup>[30]</sup> can lead to additional polysulfide anchoring by chemical absorption. The synergistic combination of both physical and chemical adsorption sites in the conductive matrix actually limits excessive polysulfide shuttle and enhance the active sulfur utilization, thus providing improved cycling stability and a high-energy density,<sup>[31,32]</sup> and possibly allowing simple synthetic pathways for potential scaling-up.<sup>[33,34]</sup> Recently, the use of biomass wastes to prepare carbonaceous materials for energy storage systems has been increasing considerably due to their abundance, accessibility, low-cost and sustainability.<sup>[35]</sup> A wide range of biomass-derived carbons from different sources, such as olive stone,<sup>[36]</sup> cherry pits,<sup>[37]</sup> banana peels,<sup>[38]</sup> brewing wastes,<sup>[39]</sup> goat hair,<sup>[40]</sup> silk cocoon,<sup>[41]</sup> luffa sponge,<sup>[42]</sup> tobacco stems,<sup>[43]</sup> among others, have been employed as stable sulfur hosts with high surface area and tuned pore size in efficient lithium batteries, including the Li-S one. A common route for improving the electrochemical response of these carbons involves activation process with the aim of modifying the porous texture and increasing their absorption properties. Chemical activations with KOH or H<sub>3</sub>PO<sub>4</sub> are among the most diffused pathways, where the latter allows the

formation of larger pores compared to the former suitable for sulfur and polysulfides hosting.<sup>[44]</sup> Indeed, pore shape and distribution into the carbon structure can play a key role in enhancing the Li-S electrochemical process. For instance, micro-pores (< 2 nm) are capable to anchor by strong interactions the soluble intermediate polysulfides, thus improving the cycling stability. Instead, meso-pores (2–50 nm) and macro-pores (>50 nm) may enable fast Li<sup>+</sup>/e<sup>-</sup> transport, shorten the diffusion pathways, and enhance the rate capability.<sup>[45]</sup> Furthermore, doping with heteroatoms such as N, O, S or P can alter the carbon framework polarity and facilitate the chemical adsorptions, thus alleviating the shuttle effect and improving the sulfur utilization.<sup>[46,47]</sup> We previously reported various activated carbon derived from biomass of different natures for Li-S batteries with promising results.<sup>[37,48–50]</sup> Herein, we use carbon substrate from mango pits, which were recently exploited to achieve high performing sulfur composites for Li cells.<sup>[51]</sup> Mango is one of the most diffused fruits with a production of more than 54 million metric tons in 2020<sup>[52]</sup> and its processing from raw fruits into finished products generates a substantial amount of waste dominated by lignocellulosic pit. These wastes can be converted into activated carbon with KOH or using H<sub>3</sub>PO<sub>4</sub>,<sup>[51]</sup> the latter used in this work to achieve a composite with S content increased both in the composite up to 90 % and in the electrode up to 6 mg cm<sup>-2</sup>, possibly benefitting from the presence of heteroatoms such as N, O, S and P as synthesis residuals. Most importantly, we focus the attention on the ion diffusion characteristics of the electrodes in Li-S cells by means of different electrochemical methods to fully understand the characteristics of this complex energy storage system, and shed light on efficient strategies to actually trigger the best performances and allow the scaling-up of cells of practical interest in terms of energy density and cycle life.

## **Results and discussion**

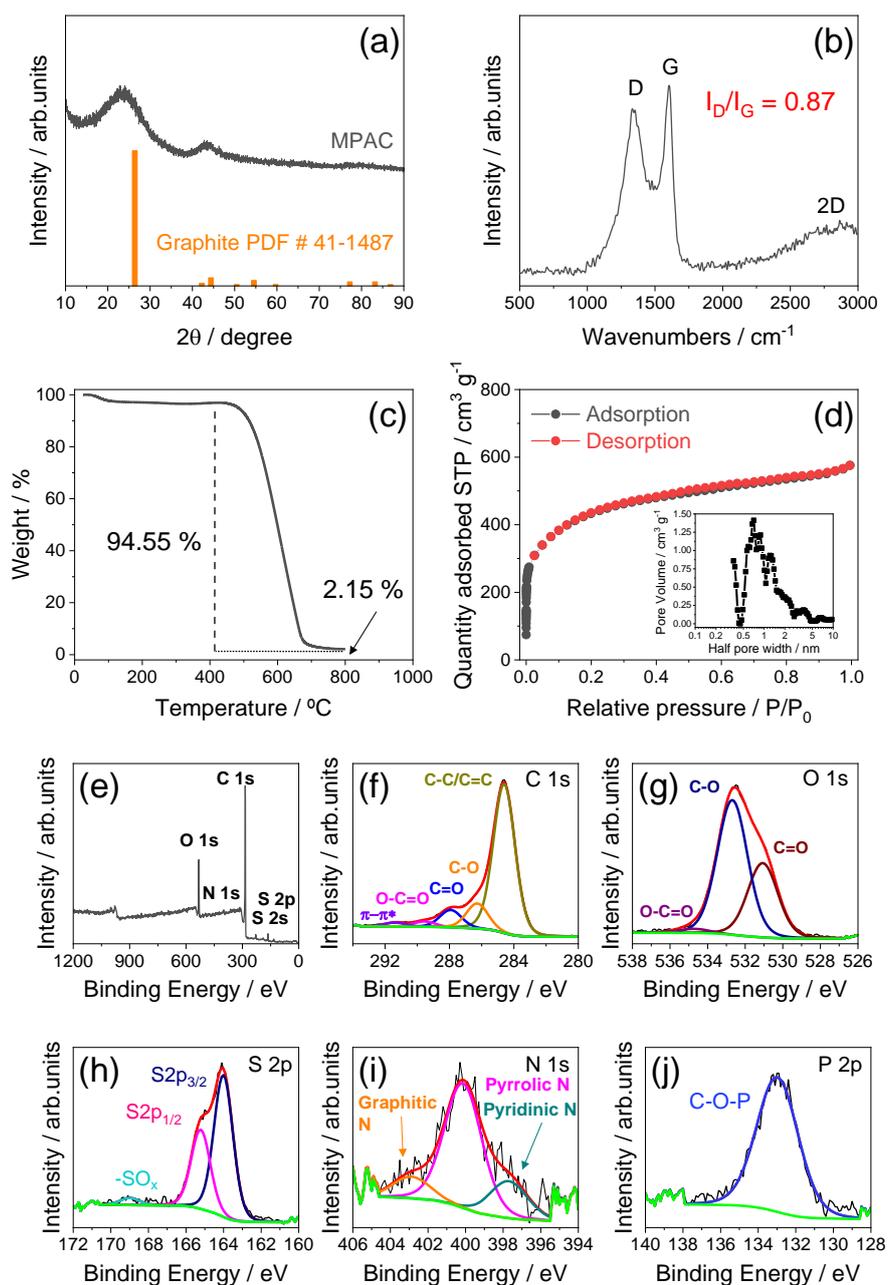
A preliminary physical-chemical investigation of the MPAC used for the preparation of the sulfur composite is reported in Figure 1. The XRD pattern in Figure 1a exhibits a relevant background and two broad peaks around 23 ° and 44 ° in  $2\theta$  range, suggesting a very limited graphitic character.

Indeed, the first peak, which is possibly indexed to the (002) plane of the natural graphite, has a relevant width, a very low intensity and a relatively high  $d$  spacing, while the second one is even less defined and may be hardly ascribed to the planes (100) and (101).<sup>[53]</sup> These features are typical of highly disordered carbons with structural hallmark of the activated carbons derived from biomass.<sup>[54]</sup> The Raman spectrum of Figure 1b agrees with the latter description of the carbon since it exhibits the two peaks around 1333 and 1603  $\text{cm}^{-1}$  assigned to  $I_D$  (forbidden in graphite) and  $I_G$ , respectively, with relatively high value of the  $I_D/I_G$  ratio (i.e., 0.87), thus suggesting a high disorder degree likely promoted by the adopted synthesis conditions.<sup>[55,56]</sup> The TGA curve of the MPAC precursor recorded under  $\text{O}_2$  atmosphere (Figure 1c) shows an initial weight loss due to absorbed  $\text{H}_2\text{O}$  (i.e., 2.8 %), a continuous weight loss between 450–750  $^\circ\text{C}$  (94.5 %) predominantly due to the combustion of the carbon matrix, and possibly organic residuals, and a final ash content of 2 %. Furthermore, the  $\text{N}_2$  adsorption/desorption isotherms of MPAC (Figure 1d) reveal the characteristic shape of a microporous solids belonging to the type I in the BDDT classification, while the almost absence of hysteresis between the two curves suggests the scarcity of mesopores as indeed confirmed by the distribution curve in inset with a pore size ranging between 0.3 and 3.0 nm.<sup>[55,56]</sup> The data of Figure 1d allow the determination of a specific surface area ( $S_{\text{BET}}$ ) of 1559  $\text{m}^2 \text{g}^{-1}$ , a micropore area ( $S_{\text{micropore}}$ ) of 1019  $\text{m}^2 \text{g}^{-1}$ , and a total pore volume ( $V_{\text{micropore}}$ ) of 0.73  $\text{cm}^3 \text{g}^{-1}$ , i.e., values expected to allow a high S content in the composite.<sup>[50]</sup> Additional characteristics of the activated carbon are given by the XPS survey spectrum in Figure 1e, which clearly shows the presence of peaks assigned to C, O, N, S and P with atomic percentage reported in Table 1, as well as a very weak signal assigned to Cl (see magnification of the low binding energy region in Figure S1 of the Supporting Material). The C 1s photoemission peak (Figure 1f) is fitted to six components attributed to the C-C bond, the C-O bonds of the hydroxy, carbonyl, and carboxyl groups, and the  $\pi-\pi^*$  transition (wake-up).<sup>[57]</sup> It is worth mentioning that the above fit neglects the interactions of C with N and S, since their energy differs within the experimental error from that of the C-O bond, although some literature possibly includes them within the C 1s signal fitting.<sup>[58,59]</sup> The O 1s peak (Figure 1g) is fitted according to three

components associated with the C functional groups discussed above.<sup>[60]</sup> Therefore, in line with the fit of the C 1s peak fitting, the most intense O 1s component corresponds to the C-O functional group, while the less intense one to the O-C=O group.<sup>[61]</sup> On the other hand, the S 2p peak (Figure 1h) reveals an intense signal ranging from 162 eV to 165 eV with a characteristic doublet assigned to the C-S bond, and a weak shoulder between 167 eV and 170 eV attributed to the S-O bond.<sup>[61]</sup> The N 1s peak (Figure 1i) fits to three components assigned to pyridinic N (397.7 eV), pyrrolic N (400.1 eV) and graphitic N (402.9 eV),<sup>[62]</sup> while the symmetrical P 2p peak centered at 133.0 eV (Figure 1j) can be fitted with a single component assigned to P-O<sup>[63]</sup> or C-O-P bonds.<sup>[64]</sup> A morphological insight on the MPAC is given by the SEM images in Figure S2 (Supporting Material) which exhibit agglomerated microparticles leading to interconnected pores, as typically observed in different activated carbons.<sup>[63-66]</sup> In addition, the EDS analysis performed on the SEM image (Figure S3) reveals, beside the carbon, the presence of O, P, S and Cl elements with amounts slightly differing from those revealed by XPS (see Table 1), while N is not detected. These apparent discrepancies are likely ascribed to the different principles on which both techniques are based. Light elements are difficult to identify in EDS because of the low energy K $\alpha$  radiation, less than 1 KeV. On the other hand, N appears as a trace element in our sample, unlike C and O, which are the predominant elements. As these three elements have similar X-ray energies (227, 392 and 525 eV for C, N and O respectively) none of the three SEM equipment used could identify the N signal.

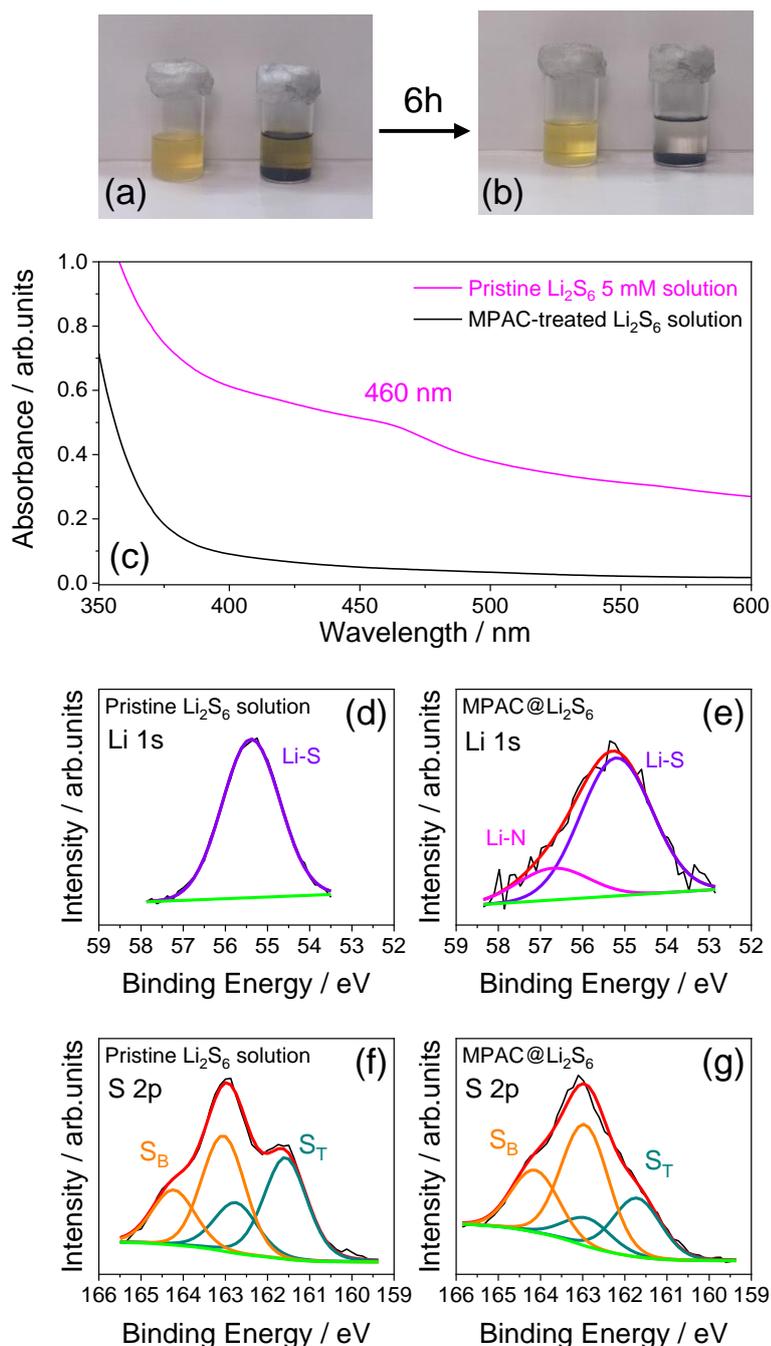
**Table 1.** Element percent concentrations detected in the MPAC sample by XPS and EDS. See Figure 1 and Figure S3 in Supporting Information, respectively, for the corresponding analyses, and experimental section for acronyms.

Element	C	O	S	N	P	Cl
XPS (at.%)	82.60	12.79	1.95	1.61	0.91	0.14
EDS (wt.%)	84.60	8.40	4.90	Not detected	1.80	0.30



**Figure 1.** Physical-chemical characterization of the MPAC sample. In detail: **(a)** X-ray diffractogram, where reference data for graphite (orange bars, PDF #41-1487) are reported for comparison; **(b)** Raman spectrum, with intensity ratio of the D and G peaks reported in inset; **(c)** TGA performed in the 25–800 °C temperature range under O<sub>2</sub> flow; **(d)** N<sub>2</sub> adsorption-desorption isotherm, inset displays the pore size distribution obtained through DFT method; **(e-j)** XPS analyses, in particular, **(e)** survey spectrum (see Figure S1 for a magnification of the low binding energy region) and **(f)** C 1s, **(g)** O 1s, **(h)** S 2p, **(i)** N 1s and **(j)** P 2p regions related spectra (the fitted line is highlighted in red color to distinguish from black experimental line). See experimental section for acronyms.

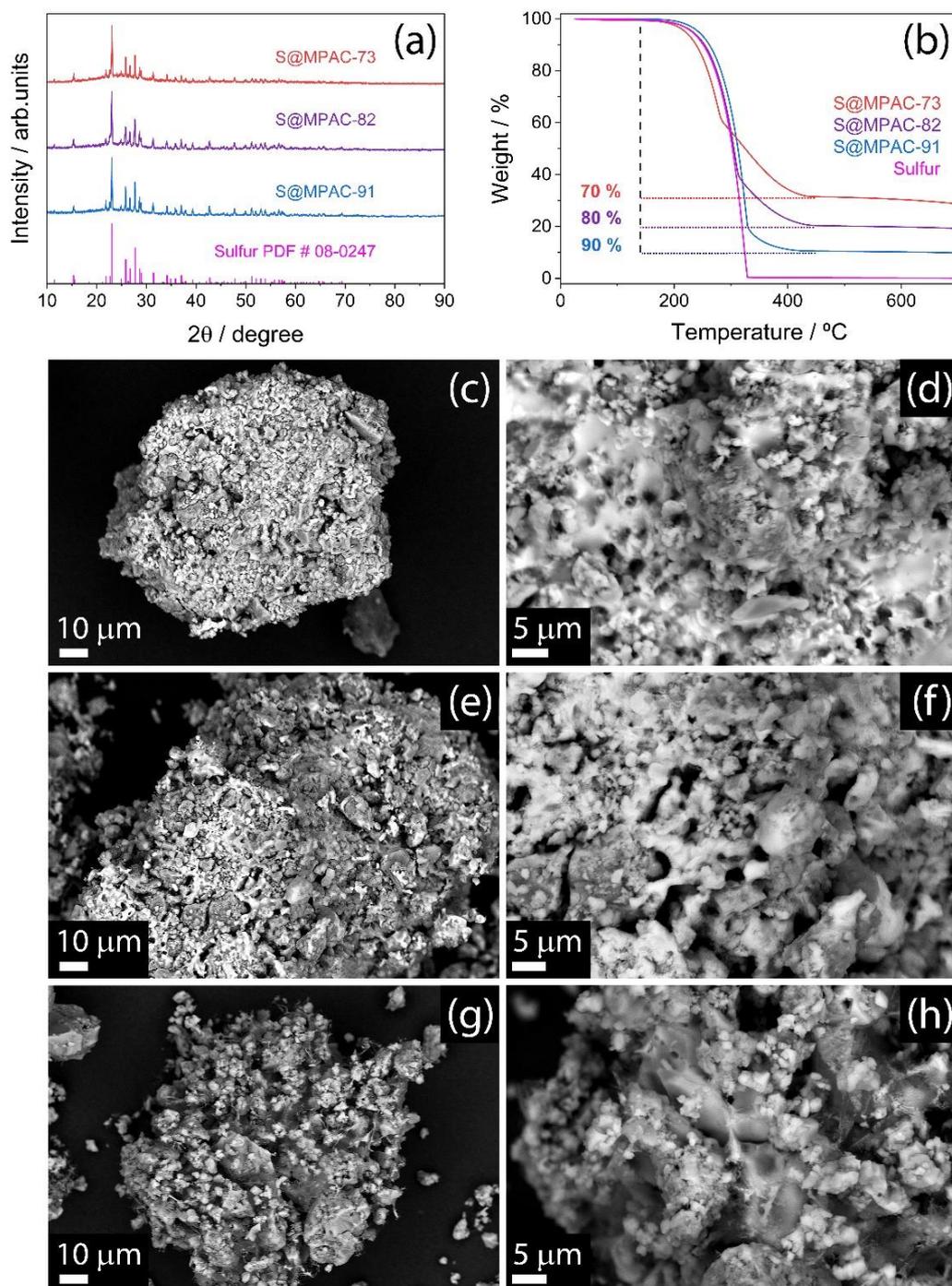
The lithium polysulfides retention ability of the MPAC is tested through UV-vis and XPS measurements carried out on a  $\text{Li}_2\text{S}_6$  solution (see preparation in Experimental section) at the pristine state and upon aging in contact with the activated carbon, as reported in Figure 2. Photographic images reveal a notable change of color of the MPAC-treated solution upon 6 hours of aging (compare Figure 2a and b) that modifies from yellow to a transparent shade indicating the absorption of the lithium polysulfides, while the pristine solution maintains its original color.<sup>[67]</sup> The polysulfides entrapment is confirmed by the UV-vis measurements performed on the  $\text{Li}_2\text{S}_6$ -containing solutions (Figure 2c) that show the vanishing of the peak ascribed to lithium polysulfides at 460 nm upon aging of the solution in contact with the MPAC.<sup>[68]</sup> XPS data obtained from the pristine  $\text{Li}_2\text{S}_6$  solution and the MPAC sample aged in contact with  $\text{Li}_2\text{S}_6$  for 6 hours (MPAC@ $\text{Li}_2\text{S}_6$ ) provide additional insight on the interaction between carbon and polysulfides (Figure 2d-g). The  $\text{Li}_2\text{S}_6$  solution at the pristine state exhibits in the Li 1s region a single signal centered around 55.4 eV ascribed to the Li-S bond (Figure 2d), while a second additional peak can be identified at about 56.6 eV for the MPAC@ $\text{Li}_2\text{S}_6$  (Figure 2e) due to the interaction between Li and the N traces in the MPAC.<sup>[69]</sup> Moreover, the S 2p spectrum of the pristine  $\text{Li}_2\text{S}_6$  solution (Figure 2f) exhibits two double-signals at 161.6 ( $\text{S}2\text{p}_{3/2}$ )/162.8 ( $\text{S}2\text{p}_{1/2}$ ) eV and 163.1 ( $\text{S}2\text{p}_{3/2}$ )/164.3 ( $\text{S}2\text{p}_{1/2}$ ) eV respectively assigned to terminal sulfur ( $\text{S}_\text{T}$ ) and bridging sulfur ( $\text{S}_\text{B}$ ) which experience significative changes in the corresponding spectra of the MPAC@ $\text{Li}_2\text{S}_6$  (Figure 2g).<sup>[68,70]</sup> Indeed, both the  $\text{S}_\text{T}$  and  $\text{S}_\text{B}$  signals shift to higher binding energies, that is, 162.9 ( $\text{S}2\text{p}_{3/2}$ )/163.9 ( $\text{S}2\text{p}_{1/2}$ ) eV and 164.0 ( $\text{S}2\text{p}_{3/2}$ )/165.0 ( $\text{S}2\text{p}_{1/2}$ ) eV, respectively, thus suggesting a decreased electron density of the sulfur atoms due to C-S interaction mainly through  $\text{S}_\text{T}$  groups.<sup>[68,69,71]</sup> The remarkable interaction of  $\text{S}_\text{T}$  with the MPAC is also evidenced by the decreased intensity of the respective signals, despite further changes of the peaks due to the presence of S traces in the MPAC cannot be excluded.



**Figure 2.** Evaluation of lithium polysulfides retention ability of the MPAC sample. In detail: **(a, b)** photographic images **(a)** at the initial stage and **(b)** after 6 hours aging of the pristine  $\text{Li}_2\text{S}_6$  solution (left-hand side) and the MPAC-treated  $\text{Li}_2\text{S}_6$  solution (right-hand side); **(c)** UV-vis measurements of the  $\text{Li}_2\text{S}_6$  solution and of the one aged in contact with MPAC for 6 hours; **(d-g)** XPS spectra related to **(d, f)** the pristine  $\text{Li}_2\text{S}_6$  solution and **(e, g)** the MPAC sample aged in contact with  $\text{Li}_2\text{S}_6$  for 6 hours (MPAC@ $\text{Li}_2\text{S}_6$ ) in the **(d, e)** Li 1s and **(f, g)** S 2p regions (the fitted line is highlighted in red color to distinguish from black experimental line). See experimental section for acronyms.

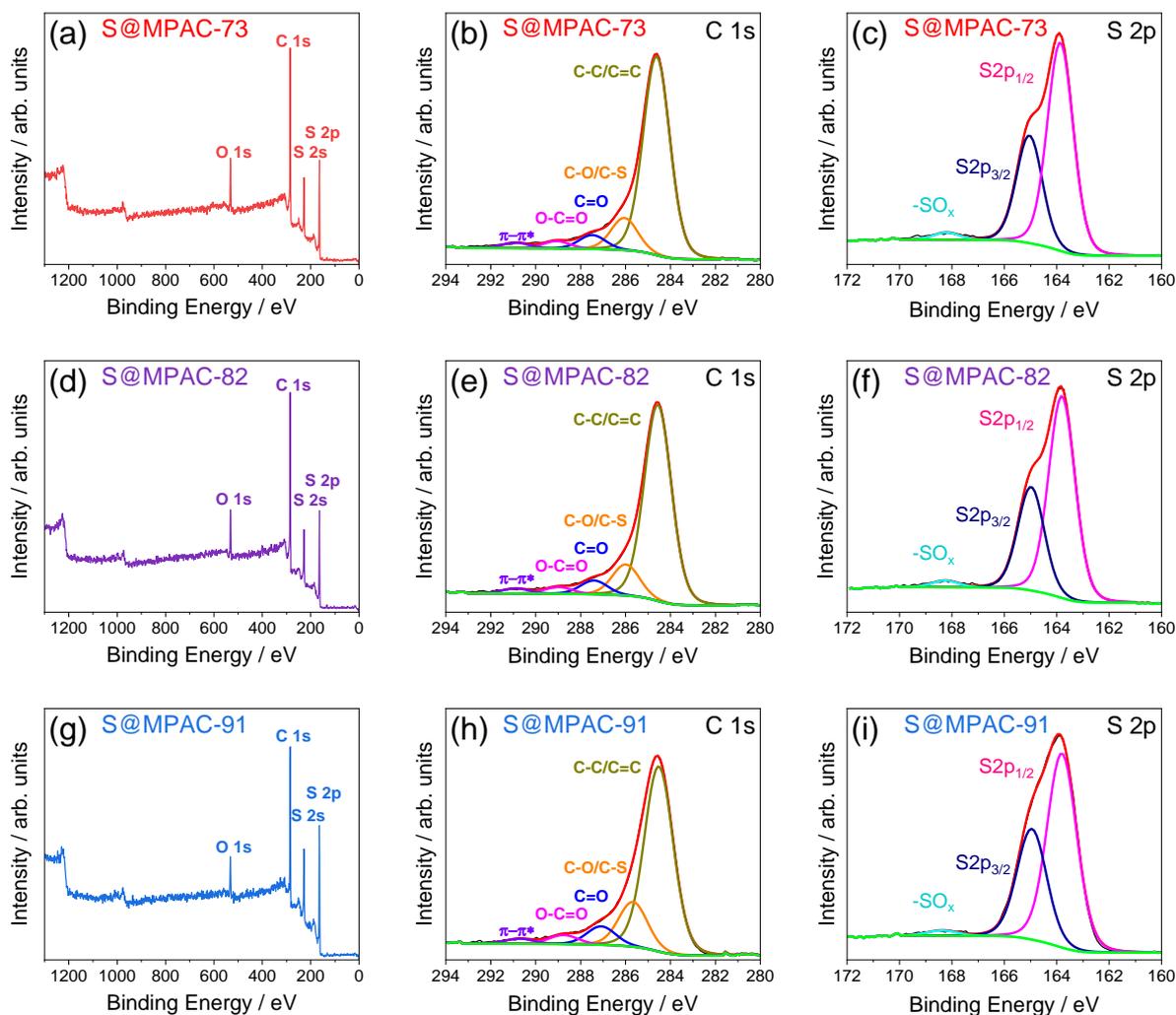
The MPAC is hereafter employed for the preparation of the sulfur composites, according to the sketch in Figure S4 (Supporting Information) which includes also the activated carbon synthesis beginning from the mango pits. It is worth mentioning that the carbonization step of the precursor to achieve the MPAC (see experimental section and left-hand side of Figure S4, Supporting Material) removes by pyrolytic decomposition the non-carbonaceous elements which are converted to volatile compounds to form multiple structural defects, thus strongly affecting the environment of the carbon atoms and giving rise to wrinkled sheets packed with a high degree of disorder as previously discussed in Figure 1. Moreover, the  $\text{H}_3\text{PO}_4$  acid promotes through surface oxidation bond cleavage to form phosphate and polyphosphates bridges that connect and crosslink the biopolymer fragments.<sup>[72]</sup> Indeed, the complete dehydration of phosphoric acid at elevated temperatures can lead to  $\text{P}_4\text{O}_{10}$  which may attack the carbon surface through the reaction scheme:  $\text{C (s)} + \text{P}_4\text{O}_{10} \text{ (g)} \rightarrow \text{P}_4 \text{ (g)} + \text{CO (g)}$ , thus leading to the development of the above discussed complex micropore system with high surface area (see Figure 1d). On the other a hand, the subsequent moderate-temperature melting-assisted sulfur incorporation into the MPAC to achieve the S@MPAC samples (see experimental section, and right-hand side of Figure S4, Supporting Material) actually represents a facile pathway suitable for avoiding side reactions that can affect the reactivity in lithium cell and, at the same time, finely tuning the sample composition, and triggering possible scalability of the electrode material.<sup>[26,34]</sup> Therefore, the synthesis allows the preparation of the three electrode materials S@MPAC-73, S@MPAC-82, and S@MPAC-91, with sulfur content increasing from 70 to 80 and to 90 wt.%, respectively, characterized in terms of structure, morphology, and composition by combining various investigation techniques in Figure 3. The XRD patterns in Figure 3a clearly exhibit the diffraction peaks of the orthorhombic S ( $\text{S}_8$ , PDF #08-0247), i.e., the most stable crystalline phase to which the molten sulfur tends to solidify back, rather than the amorphous one observed in other synthetic pathways.<sup>[73-75]</sup> Furthermore, the C component is identified by the broad peak located between  $15^\circ$  and  $35^\circ$  in  $2\theta$  range, with a decreasing intensity as the S content increases. It is worth mentioning that the absence of side peaks typical of degraded sulfur samples further suggests the mild-conditions used herein as

suitable for scaling up. The sulfur content in the composites is evaluated by thermogravimetry under N<sub>2</sub> atmosphere, and the corresponding weight losses together with that of bare S are plotted in Figure 3b. The figure likely indicates the correspondence between the initially projected S to C mass ratios (i.e., 70:30, 80:20 and 90:10) and the ones achieved for the composites after synthesis, thus indicating the almost complete absence of sulfur evaporation during the process.<sup>[76]</sup> The TGA profiles of Figure 3b, and the corresponding differential curves (DTG) reported in Figure S5 (Supporting Material), reveal significant differences. Hence, S evaporates from the composites within temperature ranging from 200 to 450 °C, instead the pure S shows an interval restricted between 200 and 330 °C. In addition, pure S shows a single TG slope (Figure 3b), represented by one peak in the corresponding DTG (Figure S5), while the composites reveal two TG slopes, with a peak and an additional high-temperature shoulder in the DTG curve having an intensity decreasing by S content increase. This trend suggests the presence of sulfur particle differently interacting with the carbon host in the composites, that is: *i*) a more volatile sulfur fraction mainly located in external shells lowly linked to carbon and represented by the peak at lower temperature in the DTG (Figure S5); *ii*) a less volatile sulfur fraction located near by the surface or within the micropores of the host in internal shells, represented by the shoulder at higher temperature in the DTG, which is more relevant at increasing carbon contents.<sup>[77,78]</sup> The morphology of the S@MPAC composites is subsequently investigated by SEM at various magnifications (Figure 3c-h). The micrographs show for all samples aggregates of sulfur and carbon with a size of about 50 μm, and an apparent porosity decreasing by increasing the sulfur content from S@MPAC-73 (Figure 3c, d) to S@MPAC-82 (Figure 3e, f) and to S@MPAC-91 (Figure 3g, h).



**Figure 3.** Physical-chemical study of the S@MPAC composites. In detail: (a) X-ray diffractograms, reference data for sulfur (magenta bars, PDF #08-0247) are reported for comparison; (b) TGA of the S@MPAC composites and elemental sulfur powder carried out under  $\text{N}_2$  flow between 25 and 700 °C (see Figure S5 in the Supporting Information for corresponding DTG); (c-h) SEM images at various magnifications of (c, d) S@MPAC-73, (e, f) S@MPAC-82 and (g, h) S@MPAC-91. See experimental section for acronyms.

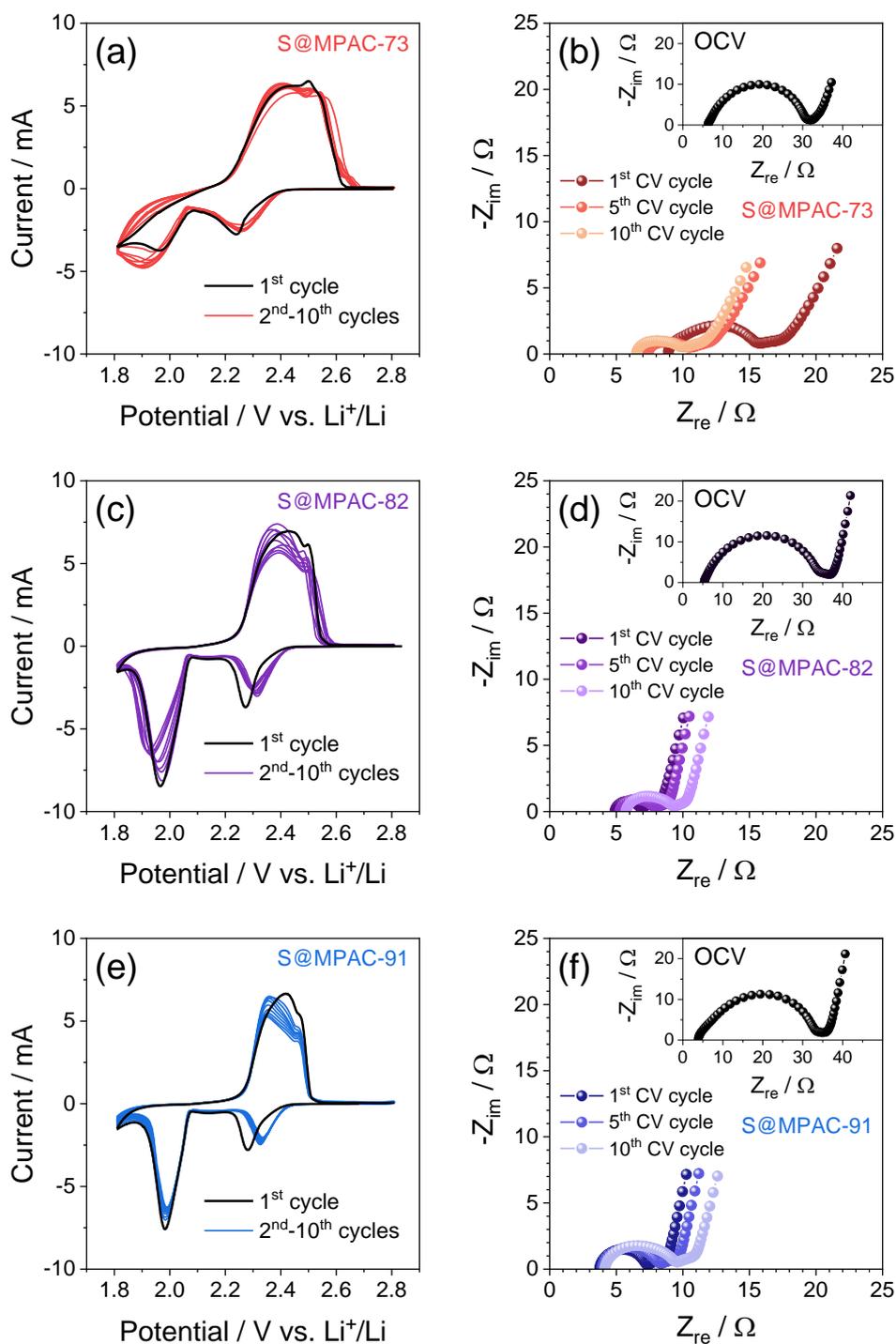
The EDS mapping included in Figure S6 (Supporting Materials) shows a very homogeneous distribution of the sulfur into the carbon matrix, with magnitude increasing by raising the sulfur content in the S@MPAC composite from 70 wt. % (Figure S6d) to 80 wt. % (Figure S6e) and to 90 wt. % (Figure S6f). The optimal structure and morphology observed in Figure 3 are expected to boost an efficient diffusion of the ions within the electrode matrix for allowing optimal operation of the Li-S cell. Furthermore, the chemical nature of the S@MPAC electrodes is investigated by XPS and the outcomes are reported in Figure 4. The survey spectra of S@MPAC-73 (Figure 4a), S@MPAC-82 (Figure 4d) and S@MPAC-91 (Figure 4g) clearly show the signals of C, O, and S. Instead, the N, P and Cl traces previously detected in the MPAC (see Figure 1 and Tab. 1) are no longer observed due to their marginal contribution which is further lowered by the predominant presence of sulfur in the composites with respect to the carbon. The XPS C 1s peaks (Figure 4b, e and h, respectively) can be likely fitted to the same components used for the MPAC host (compare with Figure 1f). The figure also evidences the intensity increase of the component assigned to the C-O bond compared to that of the C=O bond as the S content in the composite raises, particularly for S@MPAC-91 (Figure 4h), as most likely ascribed to the relevant contribution of the C-S bond. Analogously to the C 1s signal, also the S 2p peak in Figure 4(c, f, and i) shows a very a similar shape compared to the corresponding peak in the MPAC (compare with 1h). However, the intense doublet can be attributed in the composites to S-S bonds rather than C-S of the MPAC, since C-S and S-S binding energies are very similar,<sup>[61]</sup> while only traces of SO<sub>x</sub> species can be detected. The chemical features of the composites detected in Figure 4 suggest ones more the absence of side compounds that may possibly affect the Li-S cell response, cause uncontrolled increase of the overall resistance, slow down the kinetics, and negatively influence the electrode-electrolyte interphase stability, thus leading to system failures, in particular upon prolonged discharge/charge cycling.



**Figure 4.** XPS investigation carried out on the (a-c) S@MPAC-73, (d-f) S@MPAC-82, (g-i) S@MPAC-91 composites. In particular: (a, d, g) survey, (b, e, h) C 1s and (c, f, i) S 2p spectra (the fitted line is highlighted in red color to distinguish from black experimental line). See experimental section for acronyms.

The electrochemical features of the S@MPAC composites in Li-S cells are investigated by coupling cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), with the results reported in Figure 5. During the first cycle, the voltammetry curves (Figure 5a, c and e) reveal the profile expected by the conversion reaction between Li and S, with cathodic scan resolved in two well-defined reduction peaks around 2.3 and 1.9 V vs.  $\text{Li}^+/\text{Li}$  associated with the formation of high-order ( $\text{Li}_2\text{S}_x$ ,  $4 \leq x \leq 8$ ) and low-order ( $\text{Li}_2\text{S}_x$ ,  $2 \leq x \leq 4$ ) lithium polysulfides, whilst the subsequent anodic scans show the oxidation back to lithium and sulfur according to a double overlapped wave

with potential ranging from 2.1 V to 2.5 V vs. Li<sup>+</sup>/Li.<sup>[79,80]</sup> Relevantly, the three electrodes show differences in the curves shape, with a signal intensity and definition increasing and peak width decreasing by raising the S content. Indeed, S@MPAC-73 evidences the broader peaks (Figure 5a), S@MPAC-91 evidences the narrowest ones (Figure 5e), while S@MPAC-82 reveals an intermediate shape (Figure 5c), thus accounting for improving kinetics promoted by sulfur-to-carbon ratio increase. All the materials are characterized by a decrease of cell polarization upon the first cycle, with reduction peaks shifting to higher potentials and oxidation peaks to lower values, and subsequent, almost overlapped profiles with minor intensity decrease most likely due to a limited active material loss possibly occurring during the CV tests.<sup>[10]</sup> The above mentioned cell polarization decrease, which is typically indicated as *electrochemical activation process*, can be ascribed to a favorable electrode structural and morphological modifications, promoted by lithium polysulfide dissolution during discharge and subsequent sulfur deposition during charge, occurring at the first cycle.<sup>[10,11,81,82]</sup> This intriguing improvement is well justified by the EIS measurements carried out at the OCV condition of the cell and upon CV, and analyzed by non-linear least square (NLLS) method according to an equivalent circuit composed of resistive ( $R$ ) and constant phase elements (CPE,  $Q$ ), identified by the  $R_e(R_iQ_i)Q_w$  model, where  $R_e$  is the electrolyte resistance determined by the high-frequency intercept in the Nyquist plots,  $R_i$  and  $Q_i$  elements ( $R_iQ_i$ ) identify high-medium-frequency semicircles related to the electrode/electrolyte interphase, the number of which depends on the material and the considered CV cycle, and  $Q_w$  indicates the Warburg-type Li<sup>+</sup> diffusion represented by the tilted low-frequency line in the Nyquist plots.<sup>[83,84]</sup> Indeed, the results of the NLLS analysis reported in Table 2 evidence the decrease of the overall interphase resistance ( $R_{total}$ ) from about 25, 27, and 30  $\Omega$  at the OCV to about 7, 2, and 3  $\Omega$  after 1 cycle of the cells using S@MPAC-73 (Figure 5b), S@MPAC-82 (Figure 5d), and S@MPAC-91 (Figure 5f), respectively. The relevant decrease of the interphase resistance is in line with the improvement of the CV profile, while the subsequent stabilization to low hardly changing values well supports the overlapping of the subsequent voltammetry cycles.



**Figure 5.** (a, c, e) CV and (b, d, f) EIS measurements performed on Li|DOL:DME, 1 mol kg<sup>-1</sup> LiTFSI, 1 mol kg<sup>-1</sup> LiNO<sub>3</sub>|cathode cells employing either (a, b) S@MPAC-73, (c, d) S@MPAC-82 or (e, f) S@MPAC-91. CV carried out at the scan rate of 0.1 mV s<sup>-1</sup> between 1.8 and 2.8 V vs. Li<sup>+</sup>/Li; EIS performed in the 500 kHz – 0.1 Hz frequency range by applying an alternate voltage signal of 10 mV at the OCV cell condition (see related insets) and upon, 1, 5 and 10 CV cycles. See experimental section for acronyms.

**Table 2.** NLLS analyses of the Nyquist plots reported in Figure 5 recorded by EIS upon CV performed on Li|DOL:DME, 1 mol kg<sup>-1</sup> LiTFSI, 1 mol kg<sup>-1</sup> LiNO<sub>3</sub>|S@MPAC cells. Equivalent circuits and resistance values were obtained with the aid of the Boukamp software.<sup>[83,84]</sup> Only fits with a  $\chi^2$  of the order of 10<sup>-4</sup> or lower are considered acceptable. See experimental section for acronyms.

Electrode	Cell condition	Equivalent circuit	R <sub>1</sub> [Ω]	R <sub>2</sub> [Ω]	R <sub>total</sub> [Ω]	$\chi^2$
S@MPAC-73	OCV	R <sub>e</sub> (R <sub>1</sub> Q <sub>1</sub> )(R <sub>w</sub> Q <sub>w</sub> )Q <sub>w</sub>	24.8 ± 0.2	/	24.8 ± 0.2	2×10 <sup>-4</sup>
	After 1 CV cycle	R <sub>e</sub> (R <sub>1</sub> Q <sub>1</sub> )(R <sub>2</sub> Q <sub>2</sub> )(R <sub>w</sub> Q <sub>w</sub> )Q <sub>w</sub>	1.0 ± 0.2	5.5 ± 0.3	6.5 ± 0.5	1×10 <sup>-5</sup>
	After 5 CV cycles	R <sub>e</sub> (R <sub>1</sub> Q <sub>1</sub> )(R <sub>w</sub> Q <sub>w</sub> )Q <sub>w</sub>	3.2 ± 0.2	/	3.2 ± 0.2	2×10 <sup>-5</sup>
	After 10 CV cycles	R <sub>e</sub> (R <sub>1</sub> Q <sub>1</sub> )(R <sub>w</sub> Q <sub>w</sub> )Q <sub>w</sub>	3.5 ± 0.1	/	3.5 ± 0.1	2×10 <sup>-5</sup>
S@MPAC-82	OCV	R <sub>e</sub> (R <sub>1</sub> Q <sub>1</sub> )(R <sub>w</sub> Q <sub>w</sub> )Q <sub>w</sub>	26.6 ± 0.5	/	26.6 ± 0.5	7×10 <sup>-5</sup>
	After 1 CV cycle	R <sub>e</sub> (R <sub>1</sub> Q <sub>1</sub> )(R <sub>w</sub> Q <sub>w</sub> )Q <sub>w</sub>	1.9 ± 0.1	/	1.9 ± 0.1	2×10 <sup>-5</sup>
	After 5 CV cycles	R <sub>e</sub> (R <sub>1</sub> Q <sub>1</sub> )(R <sub>w</sub> Q <sub>w</sub> )Q <sub>w</sub>	2.7 ± 0.1	/	2.7 ± 0.1	4×10 <sup>-5</sup>
	After 10 CV cycles	R <sub>e</sub> (R <sub>1</sub> Q <sub>1</sub> )(R <sub>w</sub> Q <sub>w</sub> )Q <sub>w</sub>	3.6 ± 0.1	/	3.6 ± 0.1	6×10 <sup>-5</sup>
S@MPAC-91	OCV	R <sub>e</sub> (R <sub>1</sub> Q <sub>1</sub> )(R <sub>2</sub> Q <sub>2</sub> )(R <sub>w</sub> Q <sub>w</sub> )Q <sub>w</sub>	2.3 ± 0.3	27.2 ± 0.4	29.5 ± 0.7	7×10 <sup>-5</sup>
	After 1 CV cycle	R <sub>e</sub> (R <sub>1</sub> Q <sub>1</sub> )(R <sub>w</sub> Q <sub>w</sub> )Q <sub>w</sub>	3.4 ± 0.1	/	3.4 ± 0.1	5×10 <sup>-5</sup>
	After 5 CV cycles	R <sub>e</sub> (R <sub>1</sub> Q <sub>1</sub> )(R <sub>w</sub> Q <sub>w</sub> )Q <sub>w</sub>	4.2 ± 0.1	/	4.2 ± 0.1	1×10 <sup>-4</sup>
	After 10 CV cycles	R <sub>e</sub> (R <sub>1</sub> Q <sub>1</sub> )(R <sub>w</sub> Q <sub>w</sub> )Q <sub>w</sub>	5.6 ± 0.1	/	5.6 ± 0.1	8×10 <sup>-5</sup>

The diffusional characteristics study of the lithium ions into the S@MPAC electrode/electrolyte interphase represent a key aspect for fully understanding the Li-S cell features. The Li<sup>+</sup> diffusion coefficient ( $D_{Li^+}$ ) can be evaluated among several electrochemical techniques, including CV, EIS and GITT as reported in Figure 6. Indeed, the CV curves collected at various scan rates (Figure 6a-c) allows the determination of  $D_{Li^+}$  from the relationship between the peak intensity ( $I_{peak}$ ) and the square root of the potential according to the Randles–Sevcik equation (1):<sup>[81]</sup>

$$I_{peak} = 0.4463nFAC \left[ \frac{nFvD_{CV}}{RT} \right]^{1/2} \quad (1)$$

where  $I_{\text{peak}}$  is the peak current (A),  $z$  is the number of exchanged electrons of the electrochemical reaction,  $F$  is the Faraday constant (96 485 C mol<sup>-1</sup>),  $A$  is the geometric area of the electrode (1.54 cm<sup>2</sup>),  $C$  is the estimated Li<sup>+</sup> concentration in the electrode volume (mol cm<sup>-3</sup>),  $v$  is the scan rate (mV s<sup>-1</sup>),  $D$  is the diffusion coefficient (cm<sup>2</sup> s<sup>-1</sup>),  $R$  is the gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>), and  $T$  is the temperature (298 K). According to equation (1), the  $D_{\text{Li}^+}$  values obtained from CV of S@MPAC-73 (Figure 6a), S@MPAC-82 (Figure 6b), and S@MPAC-91 (Figure 6c) in lithium cell, hereafter indicated by  $D_{\text{CV}}$ , are represented by the linear slopes of the curves reporting  $I_{\text{peak}}$  and the corresponding  $v^{1/2}$ , as shown in Figure S7 (Supporting Information), where the labels 1 and 2 correspond to the reduction peaks, while 3 and 4 to the oxidation ones. It is worth noting that the differences between the potential profiles related to CV measurements at constant scan rate (Figure 5) and at increasing scan rate (Figure 6a-c) may be due to the faster activation of the interphase by the lower scan rate employed at the early stages of the latter test compared to the former one, as well as to kinetic limits occurring at the faster scan rates (see Experimental Section).

Furthermore, the analysis of the EIS Nyquist plots of S@MPAC-73 (Figure 6d), S@MPAC-82 (Figure 6e), and S@MPAC-91 (Figure 6f) in the low-frequency region allows the determination of  $D_{\text{Li}^+}$  (hereafter indicated by  $D_{\text{EIS}}$ ) at the various state of the charge (reported in insets) using equation (2):<sup>[85]</sup>

$$D_{\text{EIS}} = \frac{1}{2} \left[ \frac{RT}{z^2 F^2 C A \sigma} \right]^2 \quad (2)$$

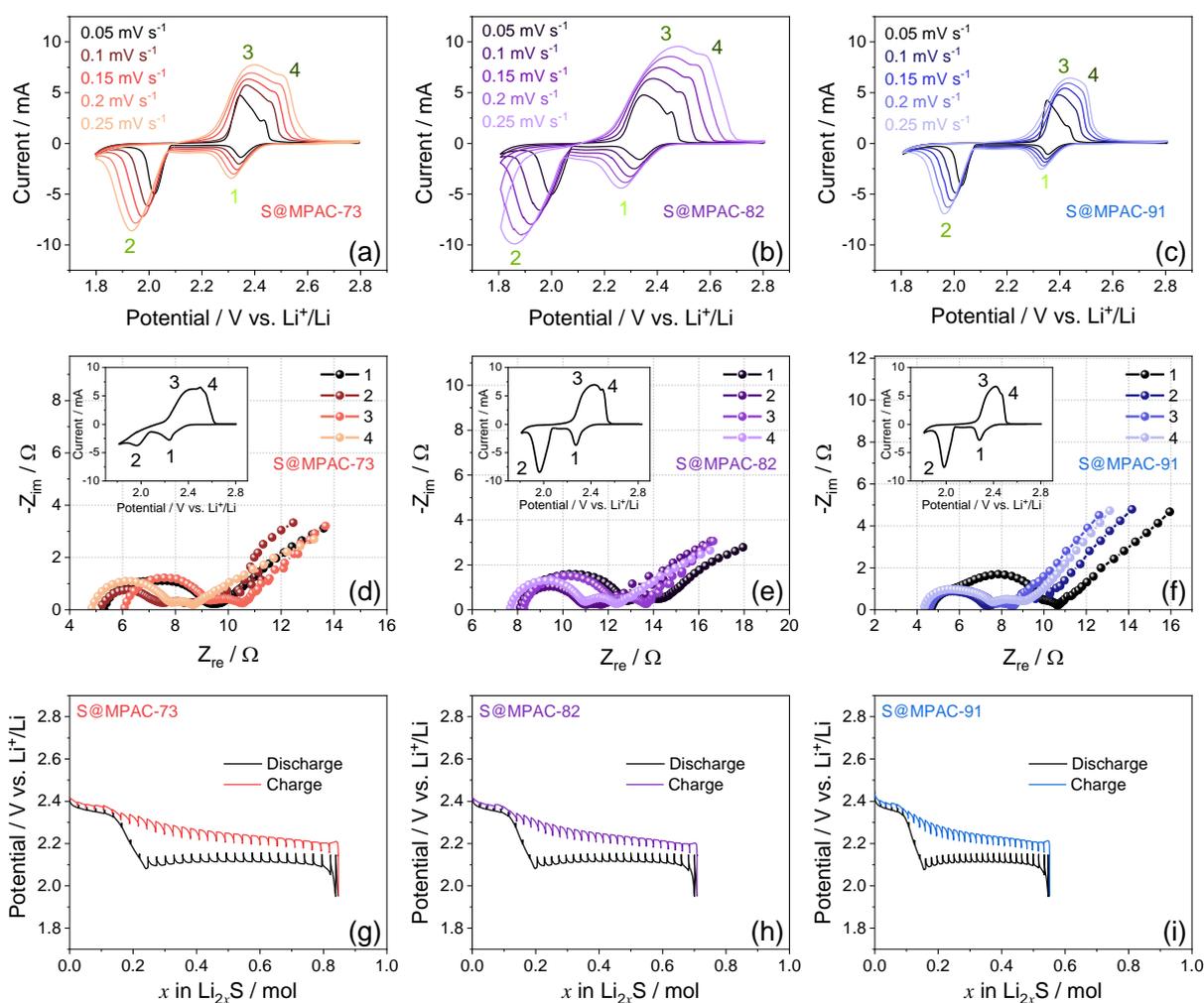
where  $R$  is the gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>),  $T$  is the temperature (298 K),  $z$  is the number of exchanged electrons in the electrochemical reaction,  $F$  is the Faraday constant (96 485 C mol<sup>-1</sup>),  $C$  is the estimated Li<sup>+</sup> concentration in the electrode volume (mol cm<sup>-3</sup>),  $A$  is the geometric area of the electrode (1.54 cm<sup>2</sup>), and  $\sigma$  is the pre-exponential factor in the equation of the complex impedance ( $Z^*$ ) vs. frequency ( $\omega$ ) within the semi-infinite diffusion condition, i.e.,  $Z_W^* = \sigma \omega^{-1/2} - j \sigma \omega^{-1/2}$  (3), which can be determined by the linear slopes of the plots reported in Figure S8 (Supporting Information) where the real and imaginary components of  $Z^*$  (i.e.,  $Z_{re}$  and  $Z_{im}$ , respectively) are

reported as function of  $\omega^{-1/2}$ . It is worth mentioning that all the electrodes reveal the Warburg-type diffusion represented by the line tilted at  $45^\circ$  in the low-frequency region of the Nyquist graphs reported in Figure 6(d-f), which allows the above mentioned linear trend of both  $Z_{re}$  and  $Z_{im}$  vs.  $\omega^{-1/2}$  at approximately constant slope ( $\sigma$ ) within the experimental error.

The lithium diffusion coefficient can be also achieved within a wide state of charge (SOC) window by GITT<sup>[86]</sup> according to a procedure widely used for Li-ion batteries,<sup>[87–89]</sup> and originally employed herein for Li–S battery. Hence, a galvanostatic titration is hereafter performed according to the details reported in the experimental section and reported in terms of potential vs.  $x$  (exchanged lithium equivalents within  $\text{Li}_{2x}\text{S}$ ) using S@MPAC-73 (Figure 6g), S@MPAC-82 (Figure 6h), and S@MPAC-91 (Figure 6i) as the working electrode in lithium cell. Indeed, the  $D_{\text{Li}^+}$ , indicated in this case as  $D_{\text{GITT}}$ , is calculated by applying equation (4):<sup>[87]</sup>

$$D_{\text{GITT}} = \frac{4}{\pi} \left[ \frac{I^0 V_M}{AF} \frac{dE/dx}{dE/dt^{1/2}} \right]^2, \quad t \ll \tau \quad (4)$$

where  $I^0$  (A) is the applied current,  $V_M$  is the sulfur molar volume of the electrode (84.48, 80.21 and 80.37  $\text{cm}^3 \text{mol}^{-1}$  for S@MPAC-73, S@MPAC-82 and S@MPAC-91, respectively),  $A$  is the electrode geometric area (1.54  $\text{cm}^2$ ),  $F$  is the Faraday constant (96 485 C  $\text{mol}^{-1}$ ),  $\tau$  is the diffusion time employed in the test(s),  $dE/dx$  is obtained by derivation of the titration plots in Figure 6(d-f), and  $dE/dt^{1/2}$  is determined by linear fitting of  $E$  vs  $t^{1/2}$  related to each current pulse (with  $t \ll \tau$ , see experimental section), exemplified for the current pulse related to  $x = 0.1$  in Figure S9 (Supporting Information). It is worth mentioning that evolution of the GITT profiles in Figure 6 fully justify the CV cycles observed previously, however in an almost thermodynamic condition, by showing an initial short reduction plateau at about 2.3 V vs.  $\text{Li}^+/\text{Li}$  during which the  $\text{S}_8$  rings break and dissolve into high-order lithium polysulfides and the potential slightly decreases, according to a single-phase transition as indeed observed by the high voltage reduction CV peak (i.e., peak 1).



**Figure 6.** Electrochemical tests performed on Li|DOL:DME, 1 mol kg<sup>-1</sup> LiTFSI, 1 mol kg<sup>-1</sup> LiNO<sub>3</sub>|cathode cells employing either (a, d, g) S@MPAC-73, (b, e, h) S@MPAC-82 or (c, f, i) S@MPAC-91. In detail: (a-c) Potential profiles related to CV carried out at increasing scan rate, the numbers label the considered potential peaks to calculate  $D_{\text{Li}^+}$  through Randles-Sevcik equation (1)<sup>[81]</sup> ( $D_{\text{CV}}$ ) (see also Figure S7 in Supporting Information and Tab. 3 for specific potentials); (d-f) Nyquist plots recorded by EIS at various states of charge during CV used to calculate  $D_{\text{Li}^+}$  by equation (2)<sup>[85]</sup>, insets show the related voltammograms and reveal the considered SOC (see also Figure S8 in Supporting Information and Tab. 3 for specific potentials); (g-i) GITT curves reported as potential vs.  $x$  (exchanged lithium equivalents within Li<sub>2x</sub>S) used to calculate  $D_{\text{Li}^+}$  through GITT equation (4)<sup>[87]</sup> (see also Figure S9 in Supporting Information and Tab. 3 for specific potentials). Square current pulses: 167.5 mA g<sup>-1</sup> (C/10 rate). Time of pulse: 987, 820, and 642 s for S@MPAC-73, SMPAC-82 and S-MPAC-91, respectively. Potential relaxation step time: 33, 27, and 21 min at OCV for S@MPAC-73, S@MPAC-82 and S@MPAC-91, respectively. Cathode sulfur loading: 2.0 mg cm<sup>-2</sup> with an area of 1.54 cm<sup>2</sup>. E/S ratio: 15 μL mg<sup>-1</sup>. Potential range: 1.95 – 2.8 V vs. Li<sup>+</sup>/Li. See experimental section for further details and for acronyms.

After a sharp decrease of the potential to about 2.1 V vs. Li<sup>+</sup>/Li, the curves show another well-defined two-phase region prolonged until the conversion into short-order lithium polysulfides (i.e., Li<sub>2</sub>S<sub>2</sub> or Li<sub>2</sub>S) upon which the voltage decreases sharply, thus accounting for the second CV reduction peak (i.e., peak 2). The subsequent oxidation reaction proceeds through specular plateaus, however with an initial process characterized by a certain slope and polarization of about 0.1-0.2 V, along a potential extending from 2.2 to 2.4 V vs. Li<sup>+</sup>/Li (corresponding to CV peak 3), and a final one about 2.4 to 2.5 V vs. Li<sup>+</sup>/Li accounting for the last CV shoulder (peak 4) due to final conversion of the polysulfides into lithium and sulfur.

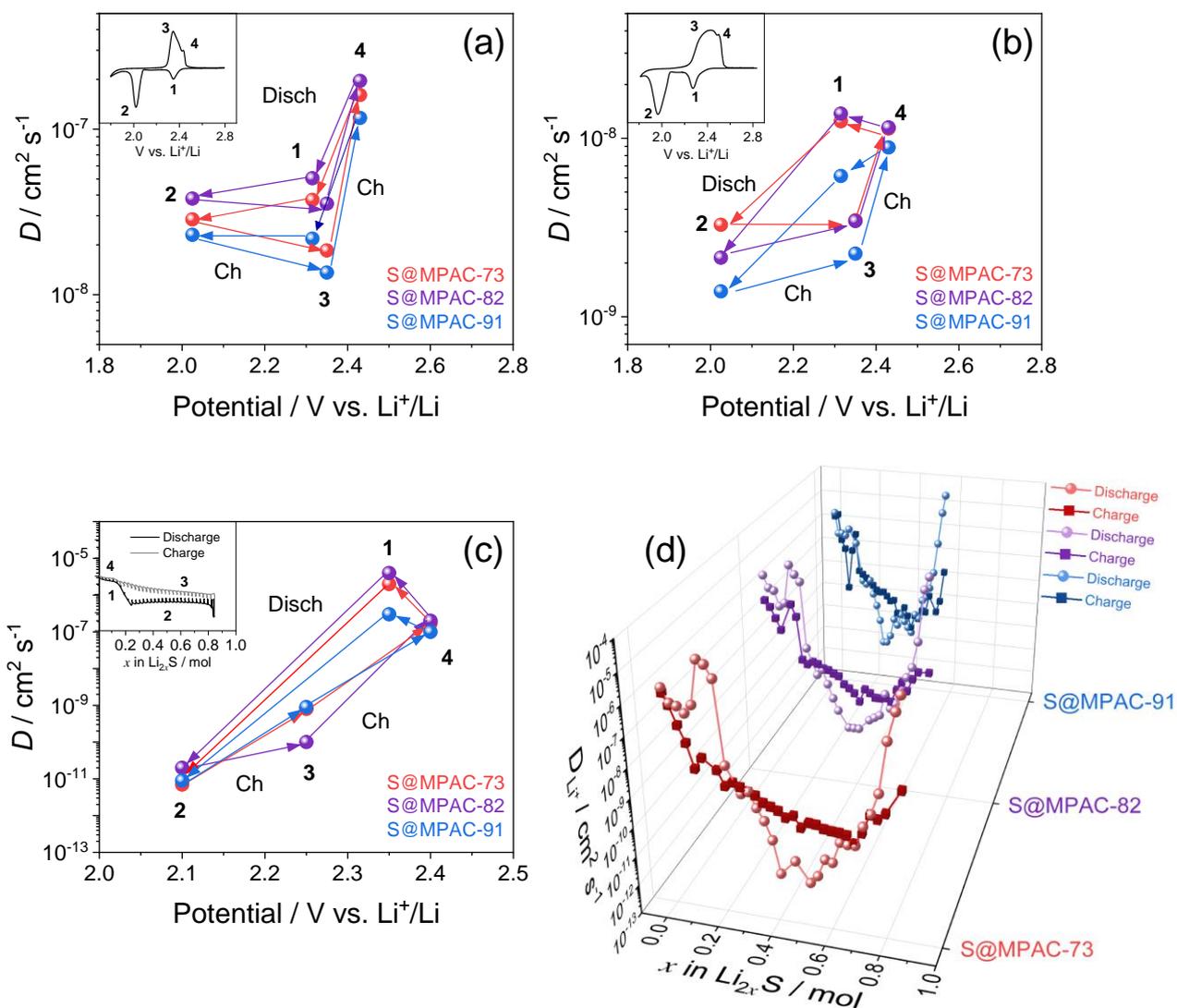
**Table 3.** Li<sup>+</sup> diffusion coefficients ( $D_{Li^+}$ ) values calculated by applying either Randles-Sevcik equation (1)<sup>[81]</sup> on CV data ( $D_{CV}$ , Figure 6a-c, and Figure S7 in Supporting Information), equation (2)<sup>[85]</sup> on EIS analyses ( $D_{EIS}$ , Figure 6d-f, and Figure S8 in Supporting Information), and GITT equation (4)<sup>[87]</sup> ( $D_{GITT}$ , Figure 6g-i, and Figure S9 in Supporting Information).

Electrode	State of charge SOC referred to CV [V vs. Li <sup>+</sup> /Li]	$D_{CV}$ [cm <sup>2</sup> s <sup>-1</sup> ]	$D_{EIS}$ [cm <sup>2</sup> s <sup>-1</sup> ]	State of charge SOC referred to GITT [V vs. Li <sup>+</sup> /Li]	$D_{GITT}$ [cm <sup>2</sup> s <sup>-1</sup> ]
S@MPAC-73	2.30 (discharge peak 1)	$3.7 \times 10^{-8}$	$1.2 \times 10^{-8}$	2.35 (discharge region 1)	$2.0 \times 10^{-6}$
	2.00 (discharge peak 2)	$2.8 \times 10^{-8}$	$3.2 \times 10^{-9}$	2.10 (discharge region 2)	$7.0 \times 10^{-12}$
	2.35 V (charge peak 3)	$1.8 \times 10^{-8}$	$3.4 \times 10^{-9}$	2.25 (charge region 3)	$8.0 \times 10^{-10}$
	2.40 (charge peak 4)	$1.6 \times 10^{-7}$	$1.1 \times 10^{-8}$	2.40 (charge region 4)	$1.7 \times 10^{-7}$
S@MPAC-82	2.30 (discharge peak 1)	$5.0 \times 10^{-8}$	$1.4 \times 10^{-8}$	2.35 (discharge region 1)	$4.0 \times 10^{-6}$
	2.00 (discharge peak 2)	$3.8 \times 10^{-8}$	$2.1 \times 10^{-9}$	2.10 (discharge region 2)	$2.0 \times 10^{-11}$
	2.35 (charge peak 3)	$3.5 \times 10^{-8}$	$3.4 \times 10^{-9}$	2.25 (charge region 3)	$1.0 \times 10^{-10}$
	2.40 (charge peak 4)	$1.9 \times 10^{-7}$	$1.1 \times 10^{-8}$	2.40 (charge region 4)	$2.0 \times 10^{-7}$
S@MPAC-91	2.30 V (discharge peak 1)	$2.1 \times 10^{-8}$	$6.1 \times 10^{-9}$	2.35 (discharge region 1)	$3.0 \times 10^{-7}$
	2.00 (discharge peak 2)	$2.3 \times 10^{-8}$	$1.4 \times 10^{-9}$	2.10 (discharge region 2)	$9.0 \times 10^{-12}$
	2.35 (charge peak 3)	$1.3 \times 10^{-8}$	$2.2 \times 10^{-9}$	2.25 (charge region 3)	$9.0 \times 10^{-10}$
	2.40 (charge peak 4)	$1.1 \times 10^{-7}$	$8.9 \times 10^{-9}$	2.40 (charge region 4)	$1.0 \times 10^{-7}$

Interestingly, Figure 6(g-i) reveals a decrease of the exchanged  $x$  value as the content of S in the composite increases, that is, from 0.83, to 0.70 and to 0.55 for S@MPAC-73, S@MPAC-82, and S@MPAC-91, respectively. Table 3 reports the  $D_{Li^+}$  values calculated from the data of Figure 6 and the Supporting Information using the various techniques and related equations, i.e.,  $D_{CV}$  (Figure 6a-c, Figure S7),  $D_{EIS}$  (Figure 6d-f, Figure S8), and  $D_{GITT}$  (Figure 6g-i, Figure S9).

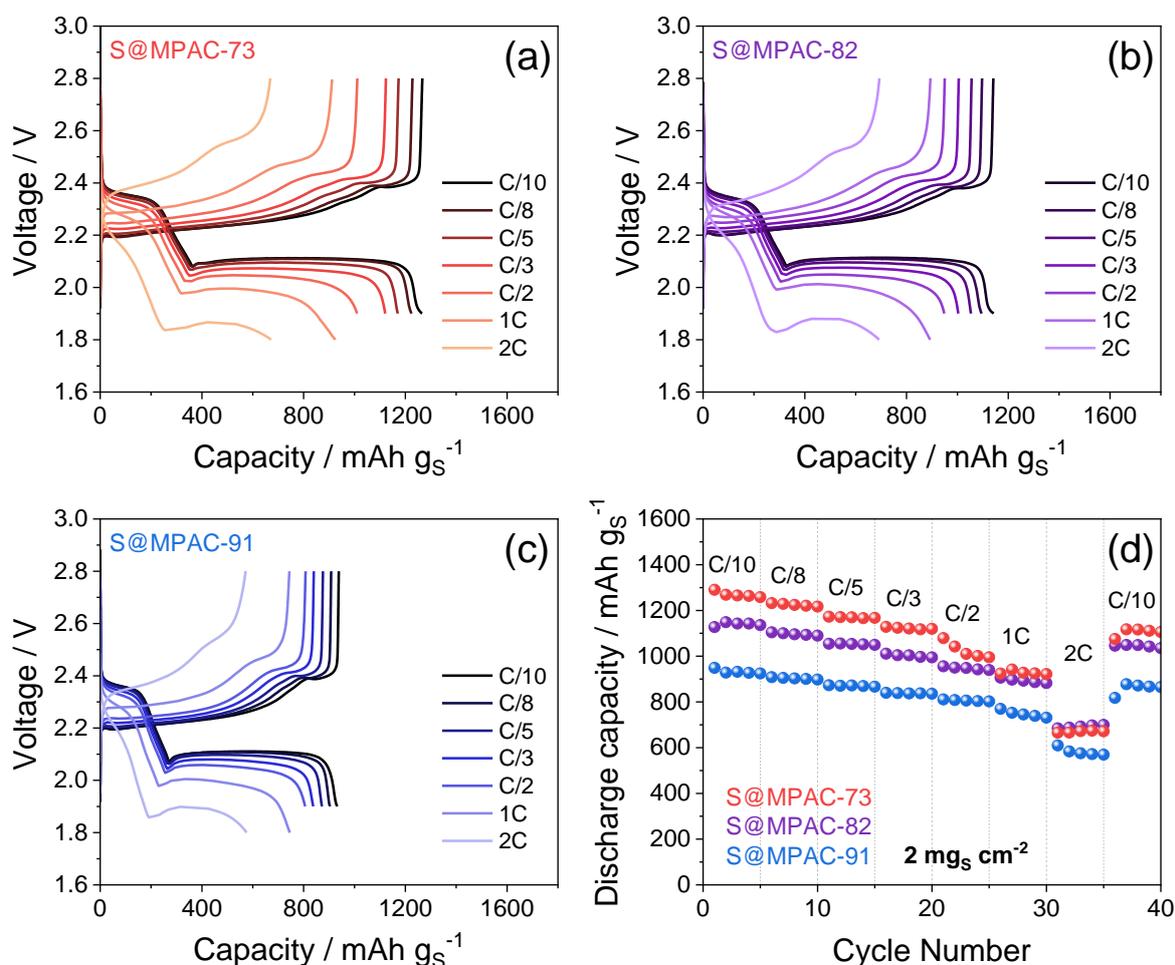
Figure 7 illustrates the plots the  $D_{Li^+}$  values according to CV (Figure 7a), EIS (Figure 7b) and GITT (Figure 7c, d) in order to investigate the effects of active material and cell SOC on the diffusion features, as well as to reveal possible influence of the experimental setup used for the study of this key parameter. For a proper comparison, the graphs in Figure 7a, Figure 7b and Figure 7c take into account the four SOC discussed previously, that is, upon first and second reduction processes (1 and 2 in inset) and after the two charge stages (3 and 4 in inset) for CV, EIS and GITT respectively. Relevantly, the figures show the dependence of  $D_{Li^+}$  trends and values on the employed technique: hence,  $D_{CV}$  ranges between  $10^{-7}$  and  $10^{-8}$   $\text{cm}^2 \text{s}^{-1}$ , as indeed observed in previous reports,<sup>[90,91]</sup> while  $D_{EIS}$  varies within one order of magnitude lower range between  $10^{-8}$  and  $10^{-9}$   $\text{cm}^2 \text{s}^{-1}$ , and  $D_{GITT}$  surprisingly shows a much wider interval between  $10^{-6}$  and  $10^{-12}$   $\text{cm}^2 \text{s}^{-1}$ . This notable variability may be ascribed to intrinsic characteristics of the technique as observed in a previous work focusing on insertion materials.<sup>[87]</sup> Indeed, CV reflects transport properties within dynamic conditions during scanning the potential, EIS allows the determination of  $D_{Li^+}$  trends in absence of significant perturbation to mitigate kinetic limits due to lithium transport, while the complex experimental setup of GITT foresees repeated current pulses and cell relaxation with a relevant effect of the employed material and cell. Meanwhile, all the techniques lead to  $D_{Li^+}$  values decreasing by the ongoing of the discharge (from state 1 to 2), due to the formation of the insoluble short-order polysulfides that may hinder the charge transfer, and increasing after charge (state 4) upon the formation of a favorable structure of the electrode in which sulfur or long-order polysulfides are intimately impregnated into the GDL and the activated carbons.<sup>[10,26]</sup> Beside similarities, Figure 7 shows that the electrode

S@MPAC-91 has mainly lower  $D_{\text{Li}^+}$  values compared to S@MPAC-73 and S@MPAC-82, likely due to the higher content of the insulating sulfur. Interestingly, the detailed GITT representation reported in Figure 7d allows the determination of the  $D_{\text{Li}^+}$  trend by the whole discharge/charge process of the cell. During discharge, the figure reveals an initial increase of the  $D_{\text{GITT}}$  from the OCV of the cell, in which crystalline sulfur is the main electrochemically active specie, to  $x$  value of 0.125 where the soluble and ion conducting  $\text{Li}_{0.25}\text{S}$  (i.e.,  $\text{Li}_2\text{S}_8$ ) is formed. The  $D_{\text{GITT}}$  drops by further discharge to reach a minimum value at  $x$  of about 0.5 for S@MPAC-73, 0.4 for S@MPAC-82, and 0.3 for S@MPAC-91, surprisingly raises again when  $x$  reaches 0.71, 0.59, and 0.44, and abruptly decreases at the end of discharge with  $x$  values of 0.83, to 0.70 and to 0.55, respectively, likely in correspondence to the formation of the most insulating species and the strong polarization at the beginning of the charge. The reverse charge curves initially evidence a further  $D_{\text{GITT}}$  decrease, and a subsequent gradual increase until the end of charge back to values comparable to those of the initial discharge states. The  $D_{\text{Li}^+}$  trends observed above indicate a strong interplay between various factors which strongly affect the ions diffusion characteristic, among them: *i*) the SOC of the cell, *ii*) the presence of conducting/insulating species in the electrode, *iii*) the morphology of the formed species during discharge/charge processes, *iv*) the adopted experimental setup which can lead to possible anisotropy of the results due to the complexity of the Li–S reactions mechanism. It is worth noting that the  $D_{\text{GITT}}$  values reported in Table 3 for the S@MPAC electrodes are comparable or even higher in the initial stage of discharge and final charged state to those of layered oxides such as LCO, NCO, NCA and NCM (L= Li; C = Co; N = Ni; M = Mn), while higher by orders of magnitude than that measured for  $\text{LiFePO}_4$ , thus suggesting the S@MPAC materials suitable for application in efficient and high rate Li–S cells.<sup>[92]</sup>



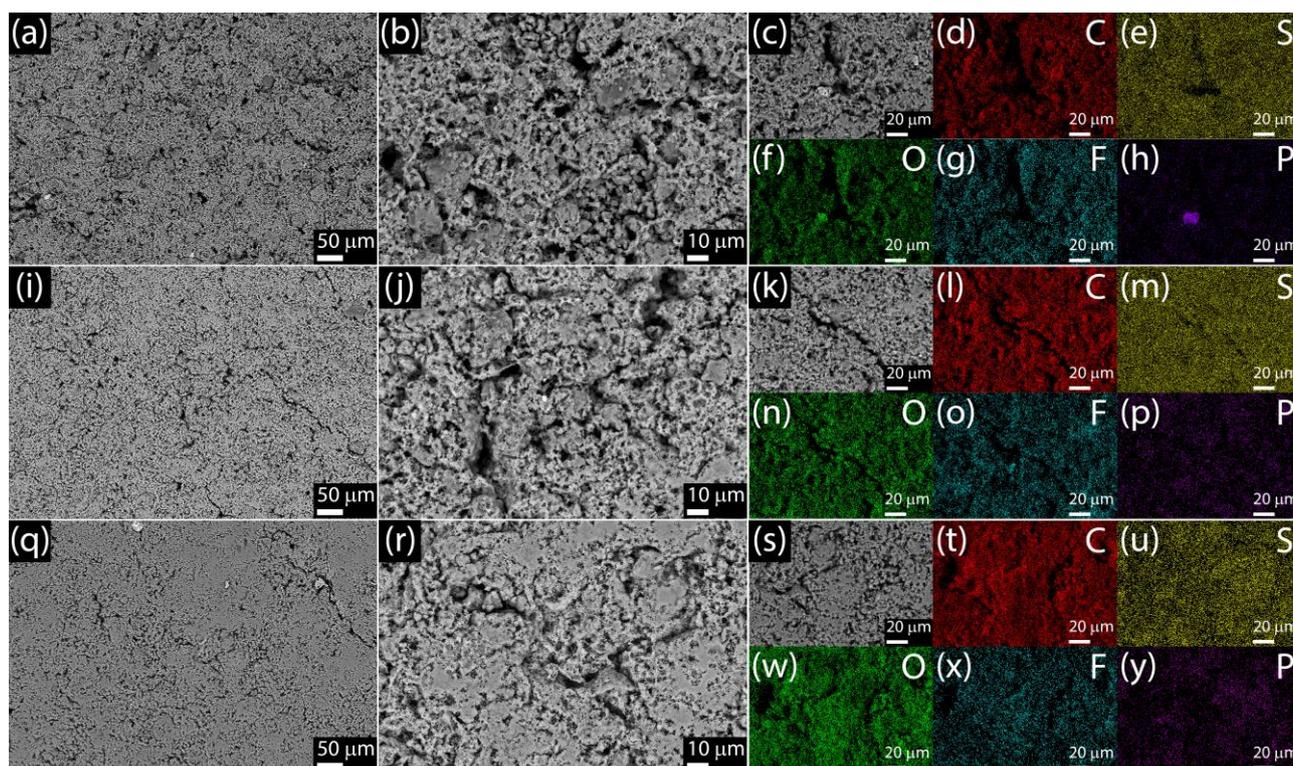
**Figure 7.** Comparison of the Li<sup>+</sup> diffusion coefficients ( $D_{Li^+}$ ) calculated through different methods, that is, **(a)** by Randels-Sevcik equation (1)<sup>[81]</sup> ( $D_{CV}$ , see Figure 6a-c, and Figure S7 in Supporting Information), **(b)** by equation (2)<sup>[85]</sup> ( $D_{EIS}$ , see Figure 6d-f, and Figure S8 in Supporting Information), and **(c)** by GITT equation (4)<sup>[87]</sup> by considering selected values obtained by the data of panel **(d)** showing the trends of the Li<sup>+</sup> diffusion coefficients values as a function of  $x$  (exchanged lithium ion within Li<sub>2x</sub>S) during the whole discharge/charge process (see Figure 6g-i, and Figure S9 in Supporting Information). Insets show the regions considered for the calculation of the  $D$  values of either voltammograms (panel **(a)** and **(b)**) or GITT curves (panel **(c)**) recorded through electrochemical tests performed on Li|DOL:DME, 1 mol kg<sup>-1</sup> LiTFSI, 1 mol kg<sup>-1</sup> LiNO<sub>3</sub>|cathode cells employing either the S@MPAC-73, S@MPAC-82 or S@MPAC-91 composites. See Tab. 3 for the selected potentials to calculate the  $D_{Li^+}$  values. See experimental section for further details and for acronyms.

Figure 8 reports the galvanostatic cycling responses of the three S@MPAC composites performed in lithium cell at currents increasing from C/10 to 2C in order to evaluate the rate capability of the materials. The voltage profiles (Figure 8a-c) reveal a shape consisting with the various steps of the redox reactions already described during the CV and GITT discussion, thus accounting for the efficiency of the reversible multi-step conversion process of lithium and sulfur to lithium polysulfides, and the fast kinetics allowed by the inclusion of the activated carbon into the S@MPAC. Indeed, the electrode stands up to a high C-rate (i.e., 2C where 1C = 1675 mA g<sub>S</sub><sup>-1</sup>) even with a sulfur content increased from 70 wt. % (Figure 8a) to 90 wt. % (Figure 8c), however with capacity decreasing due to the expected polarization increase by raising the current. The comparison of the discharge capacity as a function of the cycle number for the three composites (Figure 8d) further evidences the optimal rate capability of the materials, and shows lower values by carbon content decrease from 30 wt. % to 10 wt. % and by C-rate raise, with values of 1266, 1224, 1170, 1121, 1010, 928 and 672 mAh g<sub>S</sub><sup>-1</sup> for S@MPAC-73, 1143, 1095, 1054, 1004, 948, 893, and 672 mAh g<sub>S</sub><sup>-1</sup> for S@MPAC-82, and 932, 903, 872, 837, 806, 745, and 576 mAh g<sub>S</sub><sup>-1</sup> for S@MPAC-91 at C/10, C/8, C/5, C/3, C/2, 1C and 2C rate, respectively. This behavior accounts for the key role of the activated carbon added to the sulfur composite in boosting the reaction kinetics, despite a better practical capacity can be achieved by decreasing the carbon content due to higher content of the active material.<sup>[93]</sup> The above discussed cells are tested by employing a sulfur loading of about 2 mg cm<sup>-2</sup> as referred to the geometric area of the electrode (1.54 cm<sup>2</sup>), that is, a typical value used for material characterization, which will be subsequently increased to achieve practical cell configuration.<sup>[10,26]</sup> It is worth mentioning that the cells using S@MPAC-73, S@MPAC-82, and S@MPAC-91 recover back almost the initial discharge capacity value, i.e., 1116, 1048, and 872 mAh g<sub>S</sub><sup>-1</sup>, respectively, when the current is lowered back to the pristine value of C/10, thus indicating the stability upon the stress triggered by the continuous current raise during the tests.



**Figure 8.** (a-c) Voltage profiles and (d) corresponding cycling trends of rate capability tests carried out on Li|DOL:DME, 1 mol kg<sup>-1</sup> LiTFSI, 1 mol kg<sup>-1</sup> LiNO<sub>3</sub>|cathode cells employing either (a) S@MPAC-73, (b) S@MPAC-82 or (c) S@MPAC-91 (cathode sulfur loading: 2 mg cm<sup>-2</sup> with an area of 1.54 cm<sup>2</sup>; E/S ratio: 15 μl mg<sup>-1</sup>). Employed C-rates: C/10, C/8, C/5, C/3, C/2, 1C and 2C (1C = 1675 mA g<sup>-1</sup>) increased every 5 cycles and lowered back to C/10 after 35 cycles. Voltage ranges: 1.9 – 2.8 V from C/10 to C/2, and 1.8 – 2.8 V for 1C and 2C. See experimental section for acronyms. The cycled electrodes were retrieved upon the rate capability tests from the respective cells (see Experimental Section for details), and studied through SEM-EDS to observe their morphological retention. The SEM images reported in Figure 9 show a homogeneous porous morphology for the S@MPAC-73 (Figure 9a, b), S@MPAC-82 (Figure 9i, j) and S@MPAC-91 (Figure 9q, r) electrodes in line with the stable electrochemical performance displayed in Figure 8. Additional insights are provided by the EDS elemental maps performed on SEM images (Figure 9c, k and s) of the electrodes revealing that all three electrodes present a uniform distribution of carbon (Figure 9d, l, and t), sulfur

(Figure 9e, m and u), and oxygen (Figure 9f, n and w), alongside with fluoride deriving from the PVDF polymer binder used in the electrodes preparation (Figure 9g, o and x) and phosphorous traces ascribable to the MPAC matrix (Figure 9h, p and y). The analyses also show a decrease of surface porosity by sulfur content increase from S@MPAC-73 to S@MPAC-91, in agreement with the SEM images of the sulfur composites in Figure 3.



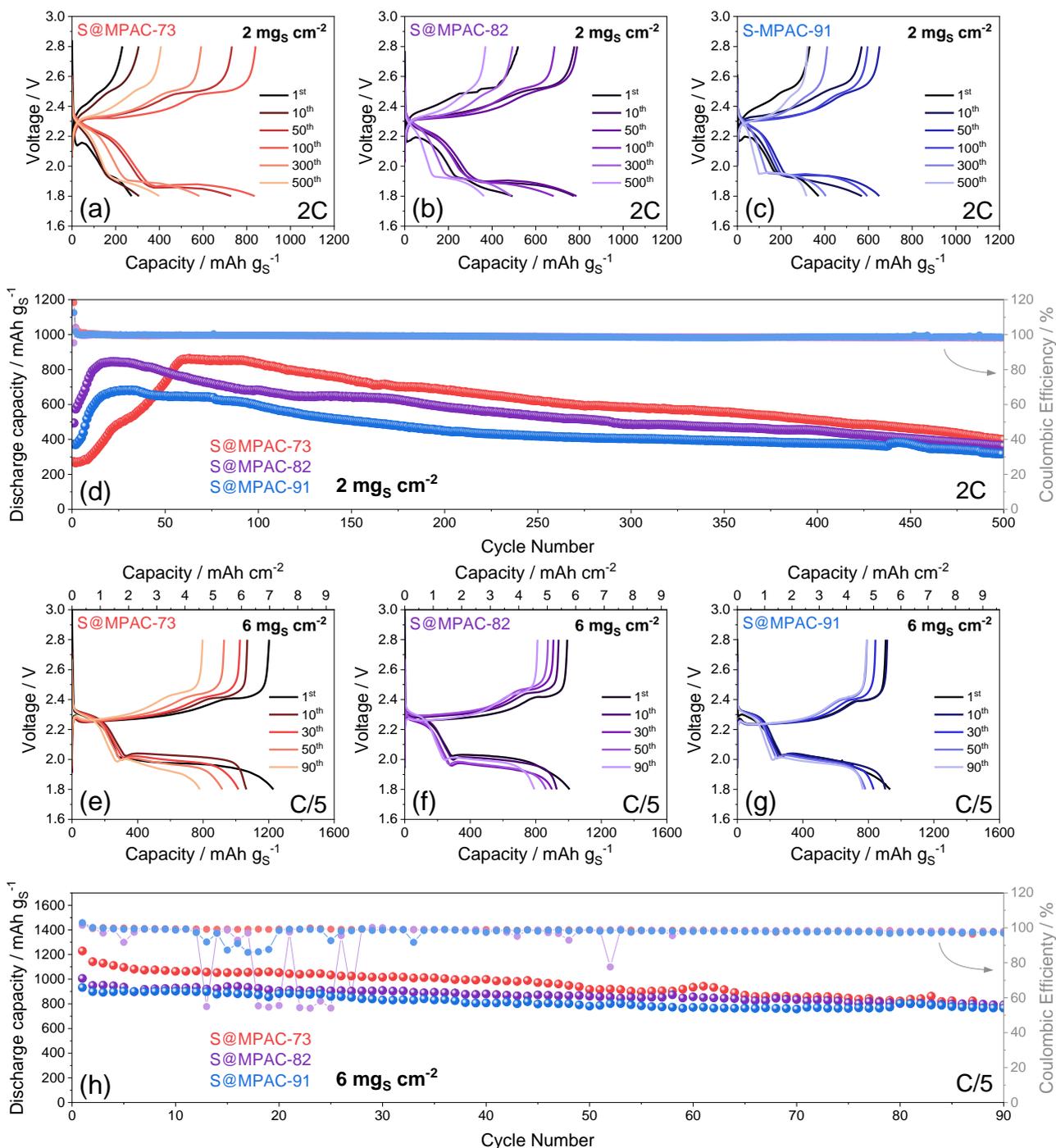
**Figure 9.** SEM-EDS analyses of the S@MPAC electrodes carried out upon rate capability tests (see Figure 8), in particular: (a, b, i, j, q, r) SEM images at various magnification of (a, b) the S@MPAC-73, (i, j) S@MPAC-82 and (q, r) S@MPAC-91 electrodes; (c, k, s) electron images and (d-h, l-p, t-y) corresponding EDS elemental maps of (d, l, t) C, (e, m, u) S, (f, n, w) O, (g, o, x) F and (h, p, y) P related to either (c-h) the S@MPAC-73, (k-p) S@MPAC-82 or (s-y) S@MPAC-91 electrode. See experimental section for details of post-mortem electrodes treatment and acronyms.

Hereafter, the S@MPAC composites are tested in lithium cell both using the sulfur loading of  $2 \text{ mg cm}^{-2}$  at the high current of 2C (i.e.,  $3350 \text{ mA g}_S^{-1}$ ) with a test prolonged over 500 cycles, and by increasing the loading to  $6 \text{ mg cm}^{-2}$  at a lower, but still effective current of C/5 ( $335 \text{ mA g}_S^{-1}$ ), with outcomes reported in Figure 10. The voltage profiles of the cells using S@MPAC-73 (Figure 10a), S@MPAC-82 (Figure 10b), and S@MPAC-91 (Figure 10c) cycled at 2C rate reveal a relatively high

polarization due to the relevant current at the initial cycles, and an activation process during the subsequent ones leading to a progressive increase of the delivered capacity, as indeed expected by the decrease of the cell impedance and polarization discussed in Figure 5 by CV and EIS. Hence, Figure 10d which reports the comparison of the cycling behavior of S@MPAC-73, S@MPAC-82, and S@MPAC-91 at 2C indicates a discharge capacity at the first cycle of about 280, 370 and 490 mAh g<sup>s</sup><sup>-1</sup> raising to about 870, 850 and 680 mAh g<sup>s</sup><sup>-1</sup>, respectively, while the coulombic efficiency approaches 100 % for all cells upon the initial cycling stages. Interestingly, the cell using the electrode with the highest carbon content (i.e., S@MPAC-73) reveals the longer activation step of 60 cycles to reach the maximum capacity with respect to the ones with lower carbon content (i.e., S@MPAC-82 and S@MPAC-91) which show instead an activation prolonged up to 20 cycles as most likely ascribed to a more relevant diffusion process of the sulfur into the carbon expected for the former with respect to the latter by the ongoing of the electrochemical conversion.<sup>[76]</sup> After the above process, Figure 10d indicates for the Li/S@MPAC-73 cell a higher delivered capacity compared to the ones using S@MPAC-82 and S@MPAC-91, thus in line with the rate capability test discussed in Figure 8. The slightly better performance in terms of delivered capacity of S@MPAC-73 compared to S@MPAC-82, and of S@MPAC-82 compared to S@MPAC-91 can be ascribed to the progressively increasing carbon content in the sulfur composites that enhances the electrodes conductivity. In addition, the trends of Figure 10d suggest a capacity retention with respect to the maximum delivered value of about 48 % for the cell using S@MPAC-91, and of about 44% for those using S@MPAC-73 and S@MPAC-82 upon the 500 charge/discharge cycles taken into account. Furthermore, the cells with sulfur loading increased up to 6 mg cm<sup>-2</sup> reveal at C/5 the proper voltage profile expected for an efficient conversion reaction occurring into S@MPAC-73 (Figure 10e), S@MPAC-82 (Figure 10f) and S@MPAC-91 (Figure 10g), with limited polarization, initial capacities of about 1220, 1020 and 940 mAh g<sup>s</sup><sup>-1</sup>, and final values of about of about 780, 790 and 760 mAh g<sup>s</sup><sup>-1</sup> upon 90 cycles, respectively. Moreover, the profiles of Figure 10(e-g) indicate a notable value of the areal capacity

(mAh cm<sup>-2</sup>) ranging from 4.5 to 7 mAh cm<sup>-2</sup> for the various electrodes. This performance can actually reflect an increased volumetric energy density value.

Therefore, Figure 10h accounts for a capacity retention increasing from 65 % for S@MPAC-73, to 79 % for S@MPAC-82, and to 80 % for S@MPAC-91, as most likely ascribed to a better electrode/electrolyte interphase triggered by the optimal cell composition in terms of overall S to C ratio and E/S ratio, the latter decreased from 15 to 10  $\mu\text{l mg}_\text{S}^{-1}$  as the sulfur loading is increased from 2 to 6 mg cm<sup>-2</sup>. The above decrease of the E/S ratio can lead to advantages in term of cell energy density and scalability, that are more relevant in Li-S cell reported in Figure S10 (Supporting Material) using the S@MPAC-91 electrode with a sulfur loading increased to 11 mg cm<sup>-2</sup> and E/S ratio decreased to 5  $\mu\text{l mg}_\text{S}^{-1}$ . The cell is cycled at C-rate lowered to C/20 in order to avoid excessive ohmic drop due to the challenging current (1C = 18 mA cm<sup>-2</sup>), and allow the operation according to the above discussed increase of the capacity upon cycling to achieve an areal value of 5 mAh cm<sup>-2</sup> (i.e., about 600 mAh gs<sup>-1</sup>). It is worth mentioning that the challenging conditions of the tests can occasionally promote partial decrease of the coulombic efficiency due to micro-dendrites formation (in particular for S@MPAC-82 in Figure 10h), however without significant effects on the cell performances as demonstrated by the satisfactory cycle life achieved by the three electrodes. Such a promising result suggests the material as viable candidate for application in effective Li-S cell with improved practical performance. Further studies in different cell configuration such as the pouch cell one can further proof the actual applicability of this system, however additional challenges ascribed to the cell assembly and geometry should be certainly taken into account.<sup>[94]</sup>



**Figure 10.** (a-c, e-g) Voltage profiles and (d, h) related cycling trends (coulombic efficiency reported on right y-axis) of galvanostatic cycling tests performed on Li|DOL:DME, 1 mol kg<sup>-1</sup> LiTFSI, 1 mol kg<sup>-1</sup> LiNO<sub>3</sub>|cathode cells employing either the (a, e) S@MPAC-73, (b, f) S@MPAC-82 or (c, g) S@MPAC-91 composites at the constant current rate of (a-d) 2C (cathode sulfur loading: 2 mg cm<sup>-2</sup> with an area of 1.54 cm<sup>-2</sup>; E/S ratio: 15 μl mg<sup>-1</sup>) and (e-h) C/5 (cathode sulfur loading: 6 mg cm<sup>-2</sup> with an area of 1.54 cm<sup>-2</sup>; E/S ratio: 10 μl mg<sup>-1</sup>, see areal capacity in mAh cm<sup>-2</sup> on top x-axis in panels (e-f)). Voltage ranges: 1.8 – 2.8 V. See experimental section for acronyms.

## Conclusions

We reported herein a study of the most relevant features with particular focus on the diffusional characteristics of a Li–S battery using an activated carbon derived from biomass (MPAC) with a high surface area and a well-defined microporous structure, suited to accommodate high active material content and allow the preparation of composites with sulfur amount of 70 wt.% (S@MPAC-73), 80 wt.% (S@MPAC-82), and 90 wt.% (S@MPAC-91). The tests indicated for the materials adequate structure, suitable morphology and chemical nature, and the absence of reactive impurities. These features allowed an efficient electrochemical process in Li–S cell, with reduction potentials of 2.1 and 1.9 V vs. Li<sup>+</sup>/Li reversed at 2.1 and 2.3 V vs. Li<sup>+</sup>/Li during oxidation, and a limited impedance decreasing from tents to units of ohms upon CV due to a favorable activation process occurring by repeated sulfur electrode dissolution and subsequent deposition. Most relevantly, the diffusion characteristics of the lithium ions have been determined using the three electrodes in the Li–S system at various SOC, and throughout different electrochemical techniques, that is, CV, EIS, and GITT. The study indicated the dependence of  $D_{\text{Li}^+}$  on the employed technique, and indicated  $D_{\text{CV}}$  ranging between  $10^{-7}$  and  $10^{-8}$  cm<sup>2</sup> s<sup>-1</sup>,  $D_{\text{EIS}}$  between  $10^{-8}$  and  $10^{-9}$  cm<sup>2</sup> s<sup>-1</sup>, and  $D_{\text{GITT}}$  between  $10^{-6}$  and  $10^{-12}$  cm<sup>2</sup> s<sup>-1</sup>. These trends accounted for the complex interplay between the SOC, the electrode nature, structure and morphology as well as the adopted experimental setup in determining the diffusional parameters of the cell. The study has shown for all electrodes the decrease of the  $D_{\text{Li}^+}$  at the end of the discharge when insulating short-order polysulfides are formed, and its increase back as the high-order ones are achieved by charge, with values of the same order or even higher compared to the most performing commercial materials projected for Li-ion battery. The electrodes revealed in lithium cell a capacity ranging from 1266 to 672 mAh g<sub>S</sub><sup>-1</sup> for S@MPAC-73, from 1143 to 672 mAh g<sub>S</sub><sup>-1</sup> for S@MPAC-82, and from 932 to 576 mAh g<sub>S</sub><sup>-1</sup> for S@MPAC-91 at current increasing from C/10 to 2C, respectively, thus accounting for the actual applicability of the carbon precursor even by increasing the sulfur contents to values as high as 90 wt. %. Prolonged tests of S@MPAC-73, S@MPAC-82, and S@MPAC-91 in lithium cells with sulfur loading of 2 mg cm<sup>-2</sup> and E/S ratio of

15  $\mu\text{l mg}_s^{-1}$  at 2C rate evidenced an activation trend with a maximum capacity of 870, 850 and 680  $\text{mAh g}_s^{-1}$ , retained for about 45 % over 500 cycles, instead cells cycled at C/5 using electrodes with loadings increased up to 6  $\text{mg cm}^{-2}$  and E/S ratio limited to 10  $\mu\text{l mg}_s^{-1}$  have shown a maximum capacity of about 1200, 1000 and 950  $\text{mAh g}_s^{-1}$  corresponding to about 5.5 ~ 7  $\text{mAh cm}^{-2}$  retained upon 90 cycles over 65, 79 and 80 %, respectively. Even more practical Li-S cell has been achieved using the most concentrated electrode (S@MPAC-91) with a sulfur loading increased up to 11  $\text{mg cm}^{-2}$  and an E/S ratio decreased to 5  $\mu\text{l mg}_s^{-1}$  with a promising geometric surface capacity of 5  $\text{mAh cm}^{-2}$ . These findings provide key information on the diffusional characteristic of the lithium sulfur cell which may actually help in rationalizing such a challenging and complex energy storage system.

## **Experimental**

### *Carbon preparation*

Mango pits were cut into pieces with a size of 1–2 cm, washed with distilled water under stirring in ambient temperature for 3 h and then dried in an oven at 120 °C in air overnight. The dried pieces were ground in a planetary ball mill (PM100 model, Retsch) at 300 rpm for 30 min using a 125 mL grinding jar with 8 stainless steel balls (10 mm diameter). Then, the obtained powder was impregnated with a solution of  $\text{H}_3\text{PO}_4$  (85 %, Panreac) in a mass ratio of 1:1 and subsequently heated in a hot plate under stirring at 85 °C for 3 h until a solid paste was obtained, which was dried at 120 °C in overnight. The impregnated product was ground again in the planetary ball mill at 300 rpm for 30 min, heated at 10 °C  $\text{min}^{-1}$  in a tubular furnace (ST-11 model, Hobersal) to 700 °C and calcinated for 2 h under a  $\text{N}_2$  atmosphere (flow rate of 50  $\text{mL min}^{-1}$ ). To remove the impurities, the sample was treated with a solution of 3 M HCl (37 %, Panreac) and heated in a hot plate under stirring at 80 °C for 3 h and then washed with distilled water until neutral pH was achieved. The resulting powder was dried in an oven in air at 120 °C for one day. The activated carbon obtained from mango pit is indicated in the work using the acronym MPAC.

### *Sulfur composites preparation*

MPAC was dried in a vacuum glass oven (Büchi) at 120 °C for 3 h and then mixed with elemental sulfur ( $\geq 99.5\%$ , Riedel-de Haën) in different S/C mass ratios, i.e., 70:30, 80:20 and 90:10. The mixtures were then heated in a silicon oil bath at 120 °C under magnetic stirring until complete melting of sulfur, and subsequently quenched to room temperature until sulfur solidification and ground in an agate mortar. The above composites were indicated with the acronyms S@MPAC-73, S@MPAC-82 and S@MPAC-91, respectively.

#### *Materials characterization*

X-ray diffraction (XRD) patterns of the carbon and the respective composites were obtained with a D8 Advance (Bruker) diffractometer equipped with a Cu-K $\alpha$  source (8.05 keV) in the range of  $2\theta$  between 10 ° and 90 ° with a step size of 0.02 ° and a scan rate of 10 s step<sup>-1</sup>. Raman spectrum of the carbon was collected with an alpha500 WITec confocal Raman spectrometer with a frequency doubled Nd:YAG (532.06 nm) laser excitation focused on the sample using a 20 $\times$ /0.4 Zeiss objective with an integration time of 1 s by accumulating a total of 10 spectra. Thermogravimetric analysis (TGA) measurements were performed through a TGA 2 Mettler-Toledo instrument in the range temperature of 25–800 °C with a heating rate of 5 °C min<sup>-1</sup> under 100 mL min<sup>-1</sup> flux of O<sub>2</sub> and N<sub>2</sub> atmospheres for the carbon and sulfur composites, respectively. The N<sub>2</sub> adsorption–desorption isotherm of the carbon was obtained with an ASAP 2020 Micromeritics porosimeter using nitrogen gas as adsorbate. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method based on nitrogen adsorption isotherm at the temperature of liquid nitrogen (77 K). The pore size distribution (PSD) was calculated using density functional theory (DFT). The scanning electron microscopy (SEM) images were obtained with a Zeiss EVO 40 microscope using a LaB<sub>6</sub> thermionic electron gun. Energy dispersive X-ray spectroscopy (EDS) microanalysis were obtained in a JEOL JSM-7800F microscope equipped with a X-ACT Cambridge Instruments analyzer. The polysulfides retention ability of the MPAC was investigated by UV-Vis spectroscopy and X-ray photoelectron spectroscopy (XPS). A 0.1 M solution of Li<sub>2</sub>S<sub>6</sub> lithium polysulfide was prepared according to a modified synthetic procedure.<sup>[95]</sup> Lithium sulfide (Li<sub>2</sub>S, 99.98% trace metals basis, Sigma-Aldrich)

and sulfur (Solvay) powders were dried under vacuum at 40 °C for 72 h and subsequently mixed in a 1:5 molar ratio in an argon sealed flask. The mixture was dispersed into a 1:1 v/v solution of 1,3-dioxolane (DOL, 99.8 % anhydrous with ca. 75 ppm BHT as inhibitor, Sigma-Aldrich) and 1,2-dimethoxyethane (DME, 99.5 % anhydrous, inhibitor-free, Sigma-Aldrich) previously stirred at 60 °C for 24 h in an Ar-filled glovebox (I-Lab 4GB, H<sub>2</sub>O and O<sub>2</sub> < 1 ppm). Afterwards, the Li<sub>2</sub>S<sub>6</sub> solution was diluted with the DOL:DME mixture to reach a concentration of 5 mM, and 5 mL of the new Li<sub>2</sub>S<sub>6</sub> solution was added to 25 mg of MPAC carbon host. After 6 hours of aging, the obtained precipitated was filtered and dried under vacuum. XPS tests were carried out on the pristine 5mM Li<sub>2</sub>S<sub>6</sub> solution and on the MPAC sample aged in contact with Li<sub>2</sub>S<sub>6</sub>, while UV-Vis measurements were performed on the pristine 5mM Li<sub>2</sub>S<sub>6</sub> solution and the one treated with the MPAC. Prior to the tests, DOL and DME solvents were dried under molecular sieves (0.3 nm, rods, size 1.6 mm (1/16 in.), Sigma-Aldrich) to reduce the H<sub>2</sub>O content and the pristine MPAC sample was dried under vacuum at 120 °C overnight. The UV-Vis spectra were recorded by using 3 mL micro-quartz cuvettes in a double beam spectrophotometer Zuzi 4260/50 model equipped with two detectors in the visible wavelength region from 350 nm to 600 nm. XPS spectra of the MPAC and S@MPAC composites were recorded with a PHOBIOS 150 MCD SPECS spectrometer with a monochromatic Mg-K $\alpha$  (1253.6 eV) radiation and a multichannel detector in a chamber able to reach a pressure of 4 $\times$ 10<sup>-9</sup> mbar. XPS spectra aimed to evaluate the polysulfides adsorption of the MPAC were obtained by using a Physical Electronic PHI VERSAPROBE spectrometer with monochromatic Al K $\alpha$  radiation (1486.6, 15 kV, 1253.6 eV) and a multi-channel detector. The energy scale of the spectrometer was calibrated using the Cu 2p<sub>3/2</sub>, Ag 3d<sub>5/2</sub> and Au 4f<sub>7/2</sub> photoelectron lines at binding energies of 932.7, 368.3 and 84.0 eV, respectively. The spectra were recorded in the constant pass energy mode at 29.35 eV, using a 200  $\mu$ m diameter analysis area. The samples were secured on a sample holder with adhesive tape and kept under high vacuum in the preparation chamber before transfer to the analysis chamber. The residual pressure in the analysis chamber was kept below

$2.0 \times 10^{-7}$  Pa during the acquisition of the spectra. Binding energy values were referred to the C 1s peak at 284.8 eV. The error in the binding energy was estimated to be about  $\pm 0.1$  eV.

#### *Electrode preparation*

The electrodes were prepared by mixing in an agate mortar the S@MPAC-73, S@MPAC-82 and S@MPAC-91 composites, respectively, with polyvinylidene fluoride (PVDF 6020, Solef ®) as the binder and carbon black (Super P, Timcal) as the conducting agent in a weight ratio of 80:10:10, using *N*-methyl-2-pyrrolidone (NMP, Sigma Aldrich) as the solvent. The obtained slurries were cast on carbon-cloth foils (GDL ELAT LT1400, MTI Corp.) through the doctor blade method (MTI Corp.). The coated films were heated on a hot plate at 50 °C in air for 3 h. The cathode electrodes were cut into 14 mm diameter disks (1.54 cm<sup>2</sup> area) and were inserted into a vacuum glass oven (Büchi) at 35 °C overnight before cell assembly in an argon-filled glovebox (MBraun, H<sub>2</sub>O and O<sub>2</sub> < 1 ppm). The electrodes were prepared into three batches with sulfur loadings of 2.0, 6.0 and 11.0 mg cm<sup>-2</sup>, with respect to the electrode geometric area of 1.54 cm<sup>2</sup>.

#### *Cell assembly, electrolyte preparation, electrochemical measurements and post-mortem analyses*

The sulfur electrodes were assembled into a CR2032 coin-cell configuration (MTI Corp.) in an argon-filled glovebox (MBraun, H<sub>2</sub>O and O<sub>2</sub> < 1 ppm) with a lithium metal disk as the counter and reference electrode (14 mm diameter), and a polyethylene separator (Celgard 2400, 16 mm diameter) soaked with the electrolyte solution. The electrolyte/sulfur (E/S) ratio to the composite electrodes was of 15, 10 and 5  $\mu\text{L mg}^{-1}$  for sulfur loading of 2.0, 6.0 and 11.0 mg cm<sup>-2</sup>, respectively. The electrolyte solution was prepared by dissolving lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 99.95 % trace metals basis, Sigma-Aldrich) and lithium nitrate (LiNO<sub>3</sub>, 99.99 % trace metals basis, Sigma-Aldrich) salts in a mixture of DOL and DME solvents (1:1, w/w ratio). The final concentration of each salt in the electrolyte solution was of 1 mol kg<sup>-1</sup> with respect to the weight of solvent (i.e., DOL:DME). LiTFSI and LiNO<sub>3</sub> salts were dried at 110 °C under vacuum in glass oven (Büchi) for 3 days, while DOL and DME solvents were dried under molecular sieves (3 Å, rod, size 1/16 in., Honeywell Fluka) and the residual moisture measured using a Karl Fischer 899 Coulometer

(Metrohm) until the water content was lower than 10 ppm. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were recorded on VersaSTAT MC Princeton Applied Research (PAR-AMETEK) analyzer. The CV was carried out within a potential range of 1.8–2.8 V vs. Li<sup>+</sup>/Li using a constant scan rate of 0.1 mV s<sup>-1</sup>, while the EIS measurements were recorded at open circuit voltage (OCV) condition and after 1, 5 and 10 CV cycles in the frequency range from 500 kHz to 100 Hz by using a 10 mV alternate voltage signal amplitude. The resulting Nyquist plots were analyzed with the non-linear least squares (NLLS) fitting method using the Boukamp software ( $\chi^2$  values suitable in the order of 10<sup>-4</sup> or lower).<sup>[83,84]</sup> The CV measurements for the lithium-ion diffusion coefficients ( $D_{Li}$ ) calculations were performed in the same potential range and under different scan rates, that is, 0.05, 0.1, 0.15, 0.2, and 0.25 mV s<sup>-1</sup>. The EIS measurements for  $D_{Li}$  calculations were recorded at the same frequency range within different electrode state of charge (SOC) obtained by linear sweep voltammetry (LSV) after a first CV activation cycle recorded at the same potential range and under a constant scan rate of 0.05 mV s<sup>-1</sup>. Galvanostatic intermittent titration technique (GITT) measurements were performed using a MACCOR series 4000 battery tester system after three activation cycles at C/10 (1C = 1675 mA g<sup>-1</sup>) in the voltage range of 1.95–2.8 V. The titrations were carried out by applying square current pulses of 167.5 mA g<sup>-1</sup> during  $t = 987, 820, \text{ and } 642$  s for S@MPAC-73, S@MPAC-82, and S@MPAC-91 electrodes, respectively, followed by potential relaxation steps of 33, 27, and 21 min at the reached OCV condition. Galvanostatic discharge-charge cycling tests were performed using a MACCOR series 4000 battery tester. Electrodes with a sulfur loading of 2 mg cm<sup>-2</sup> were tested within the current rates from C/10 to 2C (1C = 1675 mA g<sup>-1</sup>). In detail, rate capability measurements were performed under current rates at C/10, C/8, C/5, C/3, C/2, 1C and 2C increasing every 5 cycles, then returning to C/10 for the last 5 cycles. Voltage ranges of 1.9–2.8 V were used from C/10 to C/3 and of 1.8–2.8 V from C/2 to 2C during the rate capability test. Afterwards, the cells were disassembled and the electrodes retrieved, washed with DME solvent, dried under vacuum for 30 minutes at room temperature, and investigated through SEM-EDS analyses by exploiting a Zeiss EVO 40 microscope using a

LaB<sub>6</sub> thermionic electron gun (SEM) coupled with a X-ACT Cambridge Instruments analyzer (EDS). Galvanostatic measurements were also carried out for the electrodes with a sulfur loading of 2.0 mg cm<sup>-2</sup> over 500 cycles at 2C current rate within the voltage range of 1.8–2.8 V. Electrodes with a sulfur loading of 6 mg cm<sup>-2</sup> were tested over 90 cycles at a constant current rate of C/5 rate in a voltage range of 1.8–2.8 V, and electrodes with a sulfur loading of 11 mg cm<sup>-2</sup> were tested over 45 cycles at a constant current rate of C/20 in a voltage range of 1.7–2.8 V All the electrochemical measurements were performed at the controlled room temperature (25 °C).

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### **Keywords**

Diffusion process; Li-S battery; fast-kinetics; high-energy; activated carbon.

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