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Probing Charge Transport and Microstructural Attributes in Solvent- vs. Water-Based Electrodes with a Spotlight on Li-S Battery Cathode

Saeed Yari, ^{1,2,3} Liam Bird, ^{4,5,6} Sepideh Rahimisheikh, ⁷ Albin Conde Reis, ^{1,2} Mahsa Mohammad, ^{1,2} Joke Hadermann, ⁷ James Robinson, ^{5,6} Paul R. Shearing, ⁴ Mohammadhosein Safari ^{1,2,3}

¹Institute for Materials Research (IMO-imomec), UHasselt, Martelarenlaan 42, Hasselt, 3500 Belgium ² Energyville, Thor Park 8320, Genk, 3600 Belgium ³ IMEC Division IMOMEC, Diepenbeek, 3590 Belgium

⁴ The ZERO Institute, University of Oxford, Oxford, OX2 0ES, UK

⁵Electrochemical Innovation Lab, Department of Chemical Engineering, UCL, London, WC1E 7JE, UK ⁶The Faraday Institution, Quad One, Harwell Campus, Didcot, OX11 0RA, UK

⁷ Electron Microscopy for Materials Science (EMAT), University of Antwerp, Groenenborgerlaan 171, B-2020, Antwerp, Belgium

Abstract

In the quest for environmentally benign battery technologies, this study examines the microstructural and transport properties of water-processed electrodes and compares them to conventionally formulated electrodes using the toxic solvent, N-Methyl-2-pyrrolidone (NMP). Special focus is placed on sulfur electrodes utilized in lithium-sulfur batteries for their sustainability and compatibility with diverse binder/solvent systems. The characterization of the electrodes by X-ray micro-computed tomography reveals that in PVDF/NMP, sulfur particles tend to remain in large clusters but break down into finer particles in CMC-SBR/water and LiPAA/water dispersions. Our findings revealed that in the water-based electrodes the binder properties dictate the spatial arrangement of carbon particles, resulting in either thick aggregates with short-range connectivity or thin films with long-range connectivity among sulfur particles. Additionally, cracking was found to be particularly prominent in thicker water-based electrodes, propagating especially in regions with larger particle agglomerates and often extending to cause local delamination of the electrodes. These microstructural details are shown to significantly impact the tortuosity and contact resistance of the sulfur electrodes and thereby affecting the cycling performance of the Li-S battery cells.

Keywords: water-based, lithium sulfur, X-ray tomography, transport, microstructure

1. Introduction

The global pursuit of environmental goals is catalyzing the transition to battery-powered electric solutions. However, the urge for this transition should not marginalize the sustainability and environmental aspects of the battery industry. Particularly, in the manufacturing process of battery electrodes, the preparation of the electrode slurry is historically reliant on N-Methyl-2-pyrrolidone (NMP) as the solvent. Widely recognized for its toxicity and flammability,¹ as well as significant costs associated with solvent recovery in manufacture,² there are compelling grounds to seek an alternative for NMP, with water emerging as a promising candidate. The comparative life cycle assessments have shown that the transition from NMP to water for the production of battery electrodes, results in notable reductions in CO₂ equivalent emissions. ³ Furthermore, water is a cost-effective, safe and universally available solvent, rendering it a pragmatic option for scalable manufacturing. ^{4,5}

Nonetheless, the shift to water-based systems requires further adaptations, with a crucial factor being the choice of water-soluble binders to replace polyvinylidene fluoride (PVDF) which stands out as the preferred option for NMP-based slurries.⁶ The second concern relates to the possible destructive interactions between water and the active material particles. A notable example is the surface degradation of the high-Ni LiNi_xMn_yCo_{1-x-y}O₂ (NMC) particles during water processing of the cathodes for Li-ion batteries.^{7–9} The other most problematic issues are associated with the drying-induced cracking of electrodes,^{10,11} and Li leaching in water and unfavorable pH values which triggers the corrosion of aluminum current collectors. ^{12,13} Ongoing research endeavors are dedicated to addressing these challenges by using functional additives, exploration of advanced conductive agents, and surface treatment of aluminum and active material particles, among others.

The microstructure, distinguished by parameters such as particle size distribution, porosity, and tortuosity, significantly influences the transport of ions and electrons within the battery electrodes. Understanding such features is indispensable for designing the batteries exposed to challenging conditions including high current densities, low temperatures, and with thick electrodes. These aspects have been extensively studied in the literature, but primarily for the electrodes processed with NMP-based formulations with a PVDF binder. These investigations, particularly, report the

effective ionic conductivities of the porous electrodes measured by different methods including restricted diffusion experiments ^{14,15} and electrochemical impedance spectroscopy. ^{16–18} More sophisticated characterization techniques, including micro- and nano-computed tomography, ^{19,20} focused ion beam-scanning electron microscopy (FIB-SEM), ²¹ or a combination ^{22,23} have been employed to generate a more informative picture of the porous electrodes. These investigations reveal the morphology of carbon-binder domains, ^{24–26} particles' polydispersity, ^{27,28} shape, ²⁹ and their impact on the transport properties and discharge characteristics of the battery. There are other noteworthy studies such as the molecular dynamics simulations of the manufacturing steps, ^{30–32} and investigations of the formulation, architecture, ^{33–36} and calendering.³⁷ Collectively, these studies have contributed to a valuable library for deciphering microstructure and porous electrode effects, paving the way for customized electrode designs that enhance efficiency, power performance, and cycle life. ²⁰

Despite extensive research on NMP-based battery electrodes, the in-depth microstructural insights into the water-processed electrodes are scarce in the literature. This is particularly the case to a greater extent for the post-lithium-ion technologies such as the lithium-sulfur battery which has compelling advantages, including higher energy density, ample raw material availability, cost-effectiveness, and lower environmental impact.³⁸ Therefore, this study presents a comprehensive exploration of the microstructural features and transport properties of the sulfur electrodes processed from water-based slurries, contrasting them with those processed by NMP. Sulfur particles present an advantage over certain cathode active materials of Li-ion batteries, as they do not encounter the challenges posed by water contact. This feature avoids unnecessary artifacts and effects, making the system simpler to study.

2. Results and discussion

2.1. Electrochemical performance and cracking in NMP- vs. water-based sulfur electrodes

A typical lithium-sulfur (Li-S) cell is constructed with a lithium metal anode, an organic liquid electrolyte, and a composite cathode made of sulfur, carbon black, and binder. The discharge process of a Li-S cell with conventional ether-based electrolytes can be simplified in two major

parts represented by the following main transformations from the elemental sulfur (S₈) to the enddischarge products (Li_2S_2/Li_2S): ³⁹

$$\begin{split} S_8(\text{solid}) &\rightarrow \text{Li}_2\text{S}_6(\text{liquid}) \rightarrow \text{Li}_2\text{S}_4(\text{liquid}) \qquad \textit{Part I} \\ \text{Li}_2\text{S}_4(\text{liquid}) &\rightarrow \text{Li}_2\text{S}_2/\text{Li}_2\text{S}(\text{solid}) \qquad \textit{Part II} \end{split}$$

During a deep galvanostatic discharge, Part I manifests in a steep decline of the voltage ending often with a voltage dip at a capacity of Q_l whereas the Part II features a long voltage plateau with a capacity of Q_{ll} (Fig 1a-b).

In Fig 1, the discharge plots of Li-S cells during 20 galvanostatic cycles at C/10 are presented for a series of Li-S cells with different processing and formulation used in the preparation of the sulfur electrodes. The sulfur cathodes share the same composition of 60 wt.% sulfur, 30 wt.% carbon black and 10 wt.% of binder. However, they differ in the areal loadings of the sulfur, ~ 2 and 4 mg/cm², and the binder chemistry and solvent. The distinct sulfur slurries are prepared either by the NMP-soluble PVDF binder, or a water-based slurry. Here, the carboxymethyl cellulose-styrene butadiene rubber (CMC-SBR) and lithium polyacrylate (LiPAA) were used as two promising water-soluble binders. The CMC has as strong cohesive properties while SBR is a strong binder with high elasticity and flexibility. On the other hand, electrodes made with LiPAA generally have a high mechanical stability, exceptional adhesion to the aluminum current collector, and enhanced Li⁺ conductivity. ⁴⁰⁻⁴²

The discharge behavior of the PVDF-processed electrode at a loading of 2 mg/cm² exhibits a smooth discharge curve characterized by a relatively flat voltage plateau during the precipitation of the solid discharge product. The capacity starts around 1000 mAh/g and gradually decreases to 800 mAh/g over cycling. Analyzing the trends of Q_l and Q_{ll} (Fig 1c & e) is helpful to identify the sources of capacity loss. A decrease in Q_l indicates the loss of sulfur and soluble polysulfide species, while the decrease in Q_{ll} indicates a limited precipitation of the discharge products induced by the insufficiency of the carbon substrate, among other factors. However, the variations in Q_l and Q_{ll} are not completely independent and thus their ratio, hereafter defined as the conversion ratio ψ , is used for a more equitable comparison of the performance evolution of the Li-S cells over cycling (Fig 1g):

$$\psi = \frac{Q_{II}}{Q_I}$$

Notably, in the initial cycles, ψ decreases for the PVDF-processed electrodes suggesting that the capacity-loss dynamics of the cell is dominated by the hinderance to the precipitation of the solid discharge products (Fig 1g). However, this trend soon tends to stabilize, indicating that the primary cause of capacity loss is associated with the loss of sulfur or soluble products. At 4 mg/cm² sulfur loading, the behavior of the PVDF-based samples remains very similar to the 2 mg/cm² counterparts (Fig 1d, f, h). The thinner electrodes, however, at the first cycle, reveal a less distinct voltage dip between the two phases of the discharge, phases I and II (Fig 1b).

The electrode prepared with the CMC-SBR binder formulated with a water-based slurry at 2 mg/cm² of sulfur, initially demonstrates a modest Q_i capacity of approximately 200 mAh/g during the first cycle, while the Q_{II} capacity is nearly 800 mAh/q. In theory, assuming complete sulfur dissolution and the formation of Li₂S₄, the expected discharge capacities at phase I and II are Q_{l} =420 mAh/q and Q_{l} =1255 mAh/q, respectively, which correspond to a theoretical conversion ratio (ψ) of ~3. Conversion ratios below 3 suggest an inability of the conductive network to fully accommodate the solid precipitate, or its inability to fully mitigate the diffusion of soluble intermediates polysulfides from the conductive network to the negative electrode where they may undergo reduction and deposition. For the specific samples under consideration, the conversion ratio is about 4 in the first cycle, that is higher than the expected theoretical ratio (Fig 1g). A detailed examination of the voltage curve reveals that Q₁ during the initial cycle is obtained just when a voltage dip occurs. By the end of Part I, a sustained voltage recovery, which is typically observed after the voltage dip, is missing for the sulfur electrodes with CMC-SBR binder (Fig 1a). The voltage instead continuously drifts to the lower values at Part II suggesting an incomplete formation of soluble polysulfides during Part I and its concurrent formation during the precipitation of solid discharge products during Part II. At subsequent cycles, a second voltage dip gradually emerges which corroborates the belated generation of long-chain polysulfides (Fig 1a). These observations point to the microstructural obstructions to the efficient electrochemical



Fig 1. a, b) Capacity-voltage curve for cycling of NMP and water-based sulfur electrodes in Li-S cells over 20 cycles at C/10. Evolution of c & d) Q_l (discharge capacity at Part I), e & f) Q_{ll} (discharge capacity at Part II) and g &h) conversion ratio, ψ during 20 cycles. i&j) Coulombic efficiency over 20 cycles. Left columns: 2 mg/cm² sulfur loading. Right columns: 4 mg/cm² sulfur.

utilization of the sulfur particles in the pristine electrodes which become gradually accessible only after a few cycles, likely following some microstructural transformations. The incomplete dissolution of sulfur during Part I is similarly observed at the first cycle of the PVDF-based samples with a conversion ratio of marginally higher than 3, and relatively low Q_i compared to the subsequent cycles. At 4 mg/cm² sulfur loading, the CMC-SBR electrodes show a very premature end-of-discharge with large overpotential and insignificant capacity (Fig 1b). In the LiPAA-based electrodes with sulfur loadings of 2 and 4 mg/cm², after a few initial cycles with significant capacity loss, the cycling stabilizes. During cycling, Q_i shows a gradual decay, whereas Q_{ii} exhibits a significant and abrupt decline after just two cycles. This suggests that during the initial two cycles, a decisive and lasting microstructural change in the LiPAA-based electrodes happen that impedes the precipitation of solid discharge products in the subsequent cycles.

In Figs.1i & j, the Coulombic efficiency values over 20 cycles are presented, illustrating the ratio of discharge capacity to charge capacity. For the LiPAA-based electrode, similar to our observations with the conversion ratio, the first two cycles display anomalous values. In the first cycle, the discharge capacity significantly exceeds the charge capacity, indicating partial recovery and conversion of the discharge products to the sulfur during the charge step. In the second cycle, the Coulombic efficiency markedly drops to values as low as 93%. This is mainly a consequence of the significant capacity mismatch between the 2nd cycle discharge and the 1st cycle charge pointing to the incomplete sulfur utilization. This observation means that the sulfur redistribution during the first charge step renders the access to a fraction of sulfur impossible for the consequent discharge. Such a loss of cyclable sulfur is expected to mainly originate from the side reactions and the precipitation of sulfur at the electrochemically inaccessible zones. Except for the initial 2 cycles, the thin electrodes maintain a Coulombic efficiency close to 98% during further cycling, indicating highly reversible charge and discharge processes. The non-negligible difference of Coulombic efficiency between the initial and later cycles suggest that the sulfur redistribution and the concurrent microstructural evolution of the sulfur electrode is very significant at the first 2 cycles and attenuates over time. In thicker electrodes (at 4 mg/cm²), similar trends are observed for the Coulombic efficiency. It is noteworthy, however, that the contribution of the Li electrode degradation to the dynamics of the Coulombic efficiency becomes more significant for the thicker sulfur electrodes. Although both thin and thick series of electrodes were cycled at C/10, but the absolute current load on the lithium electrode is higher when thicker sulfur electrodes are cycled. This higher current density exacerbates issues such as uneven lithium plating during charging, which creates irregular, non-uniform surfaces and dendrites, resulting in dead lithium that cannot participate in subsequent cycles.^{43,44} This makes the charging phase more inefficient, impacting the Coulombic efficiency over successive cycles in cells with thicker electrode. The rate capability of the three differently processed electrodes is shown in Fig. S1. Samples made with PVDF exhibit the highest rate performance at 0.1 C, 0.2 C, and 0.5 C, followed by samples made with CMC-SBR. The samples made with LiPAA show the lowest performance. However, at 1 C, the LiPAA samples demonstrate an unusual behavior, exhibiting a higher discharge capacity. This behavior could be attributed to several factors. For example, after a few cycles, the redistribution of sulfur and changes in the microstructure may favor improved polysulfide reduction kinetics at higher charge rates. Additionally, the LiPAA-processed samples might exhibit better mechanical stability under high-rate conditions, contributing to the improved performance.

The optical micrographs from the surface of different sulfur cathodes at 2 mg/cm² show a relatively smooth surface with sporadic microcracks (Fig 2a-c). On the contrary, conspicuous large cracks appear at electrode with 4 mg/cm² of sulfur loading (Fig 2d-i). The NMP-processed electrodes experience a comparatively moderate cracking with the widest cracks below 20 μ m which do not appear to extend fully into the electrode's depth (Fig 2j and Fig S2). However, the degree of cracking is substantial for the water-based electrodes at 4 mg/cm² of sulfur loading. In these electrodes, the width of the cracks occasionally exceeds 50 μ m and cracks can penetrate all the way to the current collector-electrode interface. This observation is noteworthy for the CMC-SBR binder-based electrodes. Here, the cracks during the drying are so significant that sporadic delamination could occur at locations where the deep cracks intersect with the aluminum current collector (Fig 2k).

Drying of a wet dispersion film on a substrate is nonuniform. The evaporation of the solvent applies capillary pressure at the liquid menisci, and consequently, the air-liquid interface at all drying fronts (edge and top of the drying film) subjects the entire structure to compressive forces. In directions where there is no binding, the film shrinks freely as it dries. Nevertheless, as the adhesion of the



Fig 2. Optical images for sulfur electrodes at sulfur loadings of a-c) 2 mg/cm² and d-f) 4 mg/cm². g-i) SEM images for 4 mg/cm² sulfur electrodes, j-l) SEM cross section images for 4 mg/cm² sulfur electrodes

film to the substrate opposes the deformation in the perpendicular direction, resulting in the generation of transverse tensile stresses. Once these stresses exceed a critical threshold, the cracking initiates as a mechanism to relieve the accumulated stress.⁴⁵ Tirumkudulu and Russel derived the expression to predict the critical stress (σ_c) for nucleation of an isolated crack in a drying films: ⁴⁶

$$\frac{\sigma_c R}{2\gamma} = 0.1877 \left(\frac{2R}{h}\right)^{2/3} \left(\frac{GM\phi_{rcp}R}{2\gamma}\right)^{1/3}$$
 Eq. 2

where, *R* represents the particle radius, γ denotes the liquid-vapor surface tension of the solvent, *h* is the film thickness at cracking, *G* is the shear modulus of particles, *M* stands for the coordination number, and ϕ_{rcp} represents the particle volume fraction at random close packing. The term $\frac{\sigma_c R}{2\gamma}$ is the dimensionless critical stress which allows the comparison among different dispersions. Eq. 2 suggests that the thicker films crack at lower stresses which is in line with the higher vulnerability of the sulfur electrodes with 4 mg/cm² loading (Fig. 2). The cracking is unfavorable below a critical thickness of the film ⁴⁷ which explains the absence of severe cracking at the thinner sulfur electrodes with 2 mg/cm² loading. The dimensionless critical stress scales with the solvent surface tension according to $(\frac{1}{\gamma})^{1/3}$. As such, the substantially larger surface tension of water (72.8 mN/m at 20 °C) compared to NMP (40.8 mN/m at 20 °C) promotes higher build-up of stresses during the drying process and pronounced cracking.

2.2. X-ray tomography: linking the microstructure to the slurry properties

The three main constituents of the sulfur porous electrodes include sulfur, carbon-binder domain and pore volume. Micro-computed tomography (micro-CT) of the thick electrodes was conducted to gain a detailed three-dimensional insight into the size and spatial distribution of the electrode constituents. Two sub-volumes (cracked and uncracked) with lateral extent 0.18 x 0.18 mm (750 x 750 voxels) were analyzed for each sample to determine whether local differences existed in the sulfur and pore distribution. Five phases were identified based on X-ray attenuation, corresponding to sulfur, aluminum current collector, carbon/ binder domain (CBD), the bulk exterior, and internal pore voids in descending order of contrast (grayscale virtual slices in Fig 3b, d, and f). Due to the similar contrast of the CBD and the exterior, the sulfur particles and internal voids were retained for analysis due to the higher confidence in identifying their discrete volumes. The binarized sulfur and internal voids are shown as volume renderings in Fig. 3, where sulfur is shown in solid yellow and the internal pores are shown overlaid in translucent blue.

Fig. 4 illustrates the distribution of sulfur particles and pore sizes within the sulfur electrode, with distinct volumes represented by the equivalent diameter of a sphere with the same volume. As evident in the 3D segmented images, the size distribution of sulfur particles varies significantly across different solvent/binder systems. In samples processed with NMP, sulfur particles tend to aggregate into large clusters, particularly in areas with cracks. Conversely, water-based electrodes exhibit notably smaller sulfur particles, especially when the binder is CMC-SBR, resulting in a substantial size reduction. A comparison between cracked and uncracked regions reveals the



Fig 3. 3D segmented images obtained from the micro-CT analysis of the sulfur electrodes with different types of binder and state of cracking, corresponding to 500x500x250 voxel subvolumes: a) PVDF uncracked, b) PVDF cracked, C) CMC uncracked, d) CMC cracked, e) LiPAA uncracked, f) LiPAA cracked. Yellow volume: solid sulfur, blue volume: carbon binder domain, interstitial transparent space: bulk void and pores within electrode, overlaid on virtual slices where light contrast particles are sulfur.



Fig 4. Comparative visualization of sulfur and pore size distribution in 4 mg/cm² electrodes between NMP and water-based systems. The size distribution in the uncracked region (a) sulfur and (b) pore. The size distribution in the cracked region (c) sulfur and (d) pore.

prevalence of larger sulfur clusters in the former, prominently observed in NMP-processed samples and water-based samples with a CMC-SBR binder. When the binder is LiPAA, the particle size variation between these regions remains marginal. Additionally, the pore size distribution in NMP-processed samples differ from that in water-based electrodes, with larger pores present in the former. The variation in pore size between cracked and uncracked regions is generally insignificant, except for samples with a LiPAA binder, where cracked regions display some larger pores.

The sulfur powder tends to cluster, presenting challenges in achieving stable dispersions for the electrode slurries. The charge density in the diffuse layer (*q*) at the particle/solvent interface is a viable factor determining the stability of a solid dispersion in two respects. A higher surface charge density disfavors the formation of large particle aggregates due to the electrostatic repulsion, and hinders the sedimentation of the particles. These two related aspects of a suspension can be parametrized with the 'Zeta potential' (ζ) which is an indirect quantification of the surface charge density (*q*). Zeta potential is proportional to the charge of the surface groups and the specific adsorption at the surface of the particles as well as the solvent dielectric constant.⁴⁸ At higher absolute values of the ζ , with a conventional threshold of 30 mV, the suspension stability is expected to improve.⁴⁹ Here, ζ was measured for the sulfur, carbon, and sulfur-carbon dispersions in the water and binder solutions as a function of pH (Fig. 5). At pH values above ~5, the zeta potential for all the dispersions (Fig. 5a). The CMC-SBR-based dispersions feature very high values of $|\zeta|$ compared to the LiPAA-based dispersions (Fig. 5b). This difference is reflected in the significantly faster agglomeration and sedimentation of the sulfur particles in LiPAA/water



Fig 5. a) Variation of zeta potential (ζ) as a function of pH for the binder/solvent dispersions with solid particles comprising sulfur, carbon or both and b) the comparison of the absolute value of zeta potential among dispersions at the slurry pH (6 for CMC-SBR/water and 9 for LiPAA/water).

dispersions (Fig. S4). In this sample, the sedimentation was observed only after 4 minutes whereas the other two solvent/binder systems remained stable even after 120 minutes (Fig. S4). In LiPAA-based dispersions, the lower $|\zeta|$ is a result of interaction between the positively charged Li⁺ cations in LiPAA and the negative surface charge on sulfur, decreasing the net surface charge of the particles which deteriorates the suspension stability.

Although the zeta potential of the NMP-based dispersions was not measured due to the limitations of the experimental setup, but considerably lower values of $|\zeta|$ are expected due to the lower dielectric constant of the NMP compared to the water (78.4 vs 32.2 at 25 °C). This is also supported by the literature where $|\zeta| < 10$ mV has been reported for the sulfur/carbon black/PVDF dispersions in NMP. ⁵⁰ It is expected that sulfur gains hardly a noticeable surface charge, preserving its pristine shape in the slurry and ultimately in the porous electrode (compare Fig. 4a&c with Fig. S3).

The size distribution of the carbon-binder domain (CBD) is difficult to quantify because it consists of continuous domains spreading among the discrete sulfur particles, and also generally they fall below the resolution limits of CT. As such, the output of size-distribution analysis will be very sensitive to the user-selected input parameters as this affects the narrowest pore throat, number of domains in the final volume, and other factors that are ambiguous in a continuous domain. Therefore, an attempt was made to identify the CBD through characterization of "carbon thickness", where the distances between the surface of sulfur particles was used as a metric to gauge the thickness of carbon separating them. Additionally, the local porosity had to be included in the analysis as the interparticle distance often also includes porosity. The initial step of the analysis involved searching, within the 750×750 voxel sub-volumes, for all sulfur particles with volumes larger than particle A (Fig 6a). Subsequently, the nearest particle (particle B) with a larger volume than A was identified. Denoting the distance between the centers of these two particles as *R*, the next step was to pinpoint all pores whose centers fell within the radius *R*. Then the local porosity (i.e. porosity within the red sphere with radius *R*, Fig 6a) can be approximated by

$$\epsilon_{local} = \frac{\sum Pore \ volume \ within \ R}{\frac{4}{3}\pi R^3}$$
Eq. 3



Fig 6. a) Methodology for carbon thickness estimate. Carbon thickness as a function of local porosity, ϵ_{local} and R' for b&c) uncracked region, and d&e) cracked region of the sulfur electrodes. Height of the marginal curves indicates particle count.

The carbon thickness is then approximated as

$$t_{carbon} = (1 - \epsilon_{local}) \times R'$$

where $R'=R-r_A-r_B$ is the distance from surface of particle A to surface of particle B.

The resulting scatter plots of t_{carbon} vs ϵ_{local} and t_{carbon} vs R' are illustrated in Fig 6b-d for the uncracked and cracked regions of the sulfur electrodes. Note that as the particles are larger in the PVDF-processed sample, there are fewer data points. The probability density for the local porosity, ϵ_{local} , and the distance from a sulfur particle to a larger sulfur particle, R', are illustrated as marginal plots on the x axis (in other words, the height of the marginal plots shows the particle count at the respective x). When examining the marginal plots of ϵ_{local} (Fig 6. b&d) for both uncracked and cracked regions, it becomes evident that electrodes featuring a CMC-SBR binder incline towards higher local porosity in comparison to those with a LiPAA binder, however marginal plots of R' (Fig 6. c&e) for the two water-based electrodes tend to overlap. This observation implies that, in these two different electrodes, the variation in local porosity arise from variation of carbon thickness rather than another potential scenario where carbon with a consistent thickness occupies the space between sulfur particles of varying distance. Hence, a schematic representation can be made for the variations in t_{carbon} within a space featuring a fixed distance between two sulfur particles. This space, at low ϵ_{local} (Fig 6b, left side), is filled with a thick carbon-binder domain, whereas at high ϵ_{local} (Fig 6b, right side), only a thin carbon-binder domain is present among the sulfur particles.

A detailed investigation of marginal plots for ϵ_{local} (Fig 6. b&d) reveals that in electrodes from the LiPAA/water system, there are more instances of sulfur particle pairs with a thick carbon-binder domain, featuring 0% local porosity. This suggests a higher frequency of complete occupation of the interparticle space among sulfur particles by carbon in this electrode. Given the issues related to sulfur instability and their smaller zeta potential in the LiPAA/water solution, it is plausible that negatively charged carbon particles are more prone to align among the sulfur particles, thereby enhancing their stability (as evidenced by zeta potential values of sulfur+carbon particles in the same binder/solvent system). As a result, it is likely that these carbon particles ultimately occupy the same space within the dried electrode. In contrast, electrodes utilizing the CMC-SBR binder



Fig 7. Schematic illustration of spatial distribution of carbon-binder domain. a) in PVDF/NMP-based electrodes where sulfur particles are submerged in CBD b) in LiPAA/water-based electrodes where carbon-binder appear as a thick domain among sulfur particles, with short-range connectivity, and c) in CMC-SBR/water-based electrodes where carbon-binder appear as a thin film among sulfur particles, with long-range connectivity

exhibit numerous cases of neighboring sulfur particle with high local porosity and a thin carbonbinder domain layer. Based on these observations, we can depict the spatial arrangement of CBD within different porous electrodes as in Fig 7. Within the PVDF/NMP system, sulfur particles tend to aggregate, submerged within a bulk of CBD. Conversely, in the LiPAA/water system, sulfur avoids forming agglomerates, with CBD forming a distinct and thick domain among adjacent particles and thus exhibiting only short-range connectivity. Within the CMC-SBR system, sulfur is very finely dispersed which is also accompanied by CBD's tendency to form a uniform, thin layer enveloping particle surfaces. This CBD layer extends throughout the electrode, forming an extensive, long-range network. This variability in the spatial distribution of carbon among sulfur particles can potentially impact the transport of ions and electrons within the electrode. In the cracked regions, the spatial distribution of carbon-binder domain in the electrode with LiPAA binder remains relatively similar to the uncracked region, however when the binder is CMC-SBR, areas with high local porosity and thin carbon layer are missing, suggesting that crack tends to propagate in regions comprising thicker carbon-binder network, similar to pronounced cracking during drying of films of flocculated dispersions ⁵¹. This should be noted that, the observed arrangement of sulfur and CBD domains is for the "fresh", and "as-made" electrodes which will change during cycling.⁵²

2.3. Linking microstructure to effective transport properties and discharge performance

Within porous electrodes, the transport of electrons and ions can be hindered by a variety of internal resistances within the bulk and interfaces of the electrode. The movement of electrons is affected by the resistance at the electrode-current collector interface, resistance within the carbonbinder domain, and surface resistances of the active materials. On the other hand, the effective mobility of the charge carriers in a tortuous medium such as porous electrode is hindered compared to a bulk and homogeneous medium (e.g. free electrolyte). In this regard the intrinsic transport properties of the ionic and electronic conductor phases of a porous electrode need to be corrected by the microstructural indexes, namely the porosity (ϵ) and tortuosity (τ), to yield the effective values. Frequently, the porosity is used to estimate the tortuosity following the Bruggeman relation, e.g. $\tau = \frac{1}{e^{0.5}}$. This relation, however, is appropriate only for a homogeneous medium composed of randomly dispersed particles of the same size and underestimates the complexities of the microstructures in the battery electrodes.¹⁴ Here, the electrochemical impedance spectroscopy (EIS) of the symmetric cells made of two identical sulfur electrodes were analyzed to determine the tortuosity and contact resistance of the differently processed sulfur electrode (Fig 8a).^{17,53} Following the framework laid out in Raccichini et al.⁵³ the impedance spectra from the symmetric cells were modelled using the equivalent circuit shown in Fig 8b, where the finite-diffusion of ions through the pores coupled to the double-layer charging of the electrodeelectrolyte interface is accounted by an "open" Warburg element, Wo. The resistance of the electrolyte-filled separator is represented by R₀, and the contact resistance in the porous electrode is shown by R_1 . The impedance of the symmetric cell reads:

$$Z_{cell} = Z'_{R0} + \left(\frac{1}{\frac{1}{Z'_{R1}} + \frac{1}{Z'_{CPE1}}}\right) + Z'_{Wo}$$
Eq. 5

$$Z'_{R0} = 2 \times R0$$
 Eq. 6

$$Z'_{R1} = 2 \times R1$$
 Eq. 7

$$Z'_{CPE1} = \frac{1}{2 \times Q_{CPE}(j\omega)^P CPE}$$
Eq. 8

$$Z'_{Wo} = 2 \times R_{Wo} \times \frac{\coth[(T_{Wo}j\omega)^{P_{Wo}}]}{(T_{Wo}j\omega)^{P_{Wo}}}$$
Eq. 9

where Q_{CPE} is a constant related to the capacitance of the blocking electrode, ω is the angular frequency, P_{CPE} is the constant phase of the CPE element, R_{Wo} denotes the total resistances related to the electrolyte present in the porous electrode, T_{Wo} is a characteristic time constant and P_{Wo} is an exponent representing non-ideal capacitive behavior. A typical impedance spectrum and the resulting fit is shown in Fig 8c. The effective ionic conductivity then can be approximated by: $k_{el} = \frac{\theta}{R_{Wo}}$

where θ is the thickness of the electrode. The effective tortuosity, τ , can be estimated using the empirical MacMullin number defined as the ratio between the bulk (k_{bulk}) and effective (k_{el}) conductivities of the porous electrode:

$$N_m = \frac{k_{bulk}}{k_{el}} = \frac{\tau}{\epsilon}$$
 Eq. 11

where the value of k_{bulk} was considered to be constant and approximately equal to 10 mS.cm⁻¹ in 1M LiTFSI/DOL:DME, ^{54,55} and ϵ is the electrode porosity.

Fig 8d and e shows the values of tortuosity and contact resistance obtained by fitting the experimental EIS data to the equivalent circuit model. At thinner uncracked electrodes with a sulfur loading of 2 mg/cm², the tortuosity is relatively lower for the CMC-SBR-based samples (~2) compared to the LiPAA-based electrodes (~2.5). The tortuosity of the thicker electrodes is consistently lower than the thinner counterparts, likely attributed to the presence of large cracks providing the shortcuts for the transport of ion through the electrode thickness (Fig 8d). The electronic contact resistance at lower sulfur loading, is the smallest for the CMC-SBR-based electrodes (4 mg/cm²), a different trend is observed, where the electronic contact resistance in the CMC-SBR-based samples (~2.5). Meanwhile, for the other two types of binders, the electronic contact resistance of the electrodes with a slight decrease noted for the LiPAA-processed electrode (Fig 8e).

The effective electronic and ionic transport properties are significantly influenced by the arrangement and morphology of the carbon-binder domains in the battery porous electrodes.



Fig 8. a) Schematic of the symmetric split cell for EIS experiments, b) equivalent circuit employed for extracting tortuosity and contact resistance values from EIS measurements, c) representative Nyquist plot depicting impedance spectrum in symmetric cells. Derived values for d) tortuosity and e) contact resistance obtained through fitting experiments with the circuit model.

These microstructural details are in turn impacted by the formulation and the processing protocols such as the choice of the binder/solvent and mixing sequence, among others. In a study by Trembacki et al., ²⁴ different scenarios of carbon-binder domain morphologies were emulated for the LiNi_xMn_yCo_{1-x-y}O₂ (NMC) porous electrodes to obtain the transport properties with simulation.

The analysis included extreme scenarios, wherein carbon-binder domains exhibited thick aggregates among active material particles (known in their work as bridge-type morphology), and a thin layer uniformly covering the surfaces of the active material in the second scenario. Their findings indicate that a thick carbon-binder morphology will increase the tortuosity and electronic resistance of the electrode. On the other hand, the thin carbon-binder domain proves significantly advantageous in reducing the electronic resistance, and tortuosity. Similarly, in the electrode systems of the present study, electrode with a LiPAA binder tends to favor the formation of thick carbon-binder domains, and which proved detrimental to the tortuosity and more importantly for long-range electronic conductivity. On the other hand, the electrode with a CMC-SBR binder is more prone to developing thin layers of carbon-binder, which encouraged lower electronic contact resistance and tortuosity. Specifically, the electronic conductivity of the uncracked sample is

considerably lower, suggesting that the thin layer of carbon provides a long-range conductive network through the entire body of the electrode. In thicker electrodes processed with CMC-SBR, cracks may extend through the electrode thickness, leading to localized delamination and a significant increase in electrode contact resistance. However, such issues are absent in the PVDF/NMP system, where in thick electrodes cracks do not reach the aluminum current collector. Similarly, in the LiPAA/water system, the excellent adhesion capability of LiPAA to aluminum prevents local delamination.

Deep insights into the microstructure (Fig. 6-7) and effective transport properties (Fig. 8) of the sulfur electrodes processed with different binders facilitates the understanding of their distinct (dis)charge cycling behavior in the Li-S cells (Fig.1). The sulfur electrodes processed with PVDF/NMP exhibited a gradual capacity loss, conversion ratios within accepted and theoretical ranges, and a typical discharge curve with two distinct voltage plateaus. Notably, a characteristic voltage recovery was observed, indicative of solid product precipitation. In contrast, at 2 mg/cm² of active material loading, electrodes derived from CMC-SBR/water exhibited a more intriguing behaviors, where incomplete sulfur dissolution was detected, as evidenced by the conversion ratios surpassing theoretical values and the emergence of an additional voltage dip in the voltagecapacity plot. The pronounced dispersion of sulfur within these electrodes suggests a potential explanation: the electrolyte might struggle to reach very fine particles located in less accessible regions. This obstacle could be cleared after some discharge, triggering the volume changes within the electrode that aids the electrolyte redistribution. Moreover, the arrangement of carbon-binder domains as a thin film among sulfur particles may act as another impediment to electrolyte accessibility, essentially limiting the electrochemically active surface area until certain dischargeinduced transformations occur (low Q_1 observed in Fig 1c). Figs S5&6 show postmortem X-ray tomographic images of sulfur electrodes after a single discharge and charge cycle. Compared to the pristine samples, changes in microstructure and sulfur redistribution are clearly visible. In samples with PVDF binder, large sulfur clusters have disappeared, and sulfur is more finely distributed throughout the electrode. At crack locations, larger particles are deposited, likely due to better access to both the electrolyte and electrons. Although samples from CMC-SBR/water and LiPAA/water also exhibit large cracks, the cracks in the electrode with PVDF binder do not reach all the way to the current collector (Fig. 2d and Fig. S2). This creates possibly a "carbon valley," which is ideal for electron and ion accessibility. In the electrode from CMC-SBR/water system, sulfur is very finely distributed, but as it is resembling the pristine state it is harder to discern the sulfur redistribution.

At 4 mg/cm² of active material loading (electrode with CMC-SBR binder), the high electrode contact resistance due to local delamination, limits the discharge to very small values. Regarding the electrodes from LiPAA/water system, we observed a relatively high discharge capacity in the first cycle, which sharply declined to significantly lower values in the subsequent cycles. This phenomenon is elucidated by the arrangement of carbon-binder domains forming dense aggregates among sulfur particles. While these aggregates facilitate substantial discharge in the initial cycle by establishing a short-range network, their limited long-range connectivity proves disadvantageous. The volume changes and solid product precipitation disrupt and damage this network, resulting in a significant and swift decrease in Q_{II} values. The sulfur redistribution (Fig. S5c, and Fig. S6c) in electrode with LiPAA binder is hinting at the same conclusion, as discrete islands form in a manner similar to the formation of carbon domains in these samples. This can suggest that there are preferred local areas that are more accessible to electrons. As shown in Fig 7b, these local areas could be short-range carbon aggregates that are located among adjacent sulfur particles.

Understanding the microstructural arrangement through changes in the solvent/binder system is essential for finding potential solutions that facilitate a transition to more cost-effective and environmentally friendly manufacturing methods. From our study, we can argue that adding surfactants or surface coatings can modify the active particle surface charge, aiding in the rearrangement of the carbon-binder domain. For example, for processing of the sulfur electrodes with LiPAA binder, introducing functional groups carrying negative charge on sulfur particles, possibly can prevent the concentration of carbon particles among the sulfur particles and promote a more even distribution across the electrode. This adjustment can potentially lead to the formation of extended electronic networks, enhancing the dynamics of the discharge process in LiPAA-based electrode. To alleviate the cracking issue, a possible solution is to add co-solvents with low surface tension to water and mitigate the capillary pressure that causes the cracking.¹³

However, for a practical transition to water-based electrodes, a more comprehensive investigation is required. For instance, even after addressing electronic and ionic transport issues, we must ensure water-processed electrodes can maintain their mechanical stability over long-term cycling, especially at higher C-rates. The capacity retention of the Li-S cells at 0.5 C (Fig S7) for electrodes formulated with different binders suggests that the electrodes made from CMC-SBR/water dispersions suffer from a faster degradation. This observation likely results from an insufficient mechanical integrity of the CMC-SBR-based electrodes to accommodate rapid and large volume changes during the conversion and precipitation of the sulfur to Li₂S.

In the landscape of current research on Li-S battery electrode manufacturing, a predominant 87.2% of recent studies continue to utilize NMP as a solvent and PVDF as the binder, while a smaller yet emerging 12.8 % are opting for water-based approaches (Table S1, and Fig. S8). This stark contrast underscores the traditional reliance on NMP, a widely favored solvent due to its compatibility with various electrode materials. However, the shift towards water-based methods represents a significant departure in terms of environmental impact and economic feasibility. For Li-ion batteries, it has been demonstrated that while only 4.6% of the cost of manufacturing is due to solvent recovery, a significant 46.84% of the total energy consumption is consumed by drying and solvent recovery steps because of the high boiling point of the organic solvent NMP, which is an environmental drawback.⁵⁶ Therefore, transitioning to water-based slurries could substantially reduce both carbon footprints and capital costs.⁴ Given the significant similarities in cost and energy consumption during the cathode manufacturing steps of Li-S and Li-ion batteries,⁵⁷ Li-S batteries can also greatly benefit from shifting to water-based processing. While the dominance of NMP in current research reflects its established effectiveness, the increasing adoption of waterbased alternatives signals a promising trend towards greener and more sustainable battery manufacturing technologies. Future research should continue to explore and refine water-based methods to enhance their efficiency and applicability across various battery types and configurations, thereby fostering a more sustainable and environmentally conscious approach to energy storage technology.

3. Conclusion

This study systematically investigated the microstructure and transport properties of NMP versus water-based sulfur electrodes for lithium-sulfur batteries. PVDF binder was chosen for NMP-based electrodes, while water-based electrodes were fabricated with two different binders, CMC-SBR and LiPAA. Detailed microstructural information, including particle and pore size distribution, as well as the spatial arrangement of carbon-binder domains, was obtained through X-ray microcomputed tomography. Exploring the intricate links between microstructure and transport properties, the study employed electrochemical impedance spectroscopy on symmetric cells with identical sulfur electrodes to determine electronic contact resistance and electrode tortuosity, a crucial factor influencing effective ionic conductivity. The results uncovered significant differences in particle size distribution, tortuosity, and contact resistance among various samples, underscoring the substantial impact of binder and solvent selection. Water, as a solvent, enabled a high Zeta potential for the dispersions, preventing close contact among sulfur particles and causing them to disperse into fine particles, a phenomenon not observed with NMP. On the other hand, binder selection played a pivotal role in shaping carbon-binder domain morphologies, affecting tortuosity, and electronic resistance. The CMC-SBR binder facilitated the arrangement of carbon-binder domains as thin layers with long-range connectivity, resulting in lower electronic contact resistance. Conversely, LiPAA binder encouraged the formation of thick carbon domains among sulfur particles with only short-range contact, thereby increasing electronic contact resistance and electrode tortuosity. In thick electrodes, water exhibited a distinct influence on transport properties, introducing large cracks during electrode drying due to its high surface tension that raises capillary pressure. These cracks led to local electrode delamination, ultimately compromising electronic conductivity. The interplay of these characteristics significantly influenced cell discharge behavior. Factors such as accessibility of the particles for electrochemical reaction, contact resistances in the electrode or the capability of the carbon-binder network to remain intact and undisrupted during discharge, shaped the dynamics of cell discharge. These findings provide valuable insights for optimizing the design of water-based electrodes, emphasizing the importance of a comprehensive understanding of the intricate relationships between binder choice, microstructure, and electrochemical performance.

4. Experimental procedures

4.1. Materials, cell assembly and electrochemical testing

Sulfur cathodes were prepared using a mixture of sulfur powder (VWR, mesh 325), carbon black (Imerys Carbon and Graphite, C45), and a binder solution. The binder solutions were composed of PVDF (Solef 5130, Solvay) in NMP, CMC-SBR (50:50) in water, or LiPAA in water. The binder solution was prepared by dissolving 2 wt.% CMC (Alfa Aesar) in water using a planetary mixer. The SBR was obtained as an aqueous solution containing 50% solids (MTI group). The quantities of these two solutions were precisely adjusted in the slurry to maintain a 50:50 ratio of the binders in the dispersion. Lithium polyacrylate (LiPAA) was prepared by neutralizing a polyacrylic acid solution (35 wt.%, Sigma-Aldrich, $M_v \approx 250,000$) with a lithium hydroxide (LiOH) solution (2 mol/L) until the pH reached approximately 9. The resulting LiPAA solution was then adjusted to a final concentration of 10 wt.% by addition of deionized water. The ratio of active material to carbon to binder in the solid part of the slurry was consistently set at 60:30:10. The mixing process was carried out in a ball miller (Emax-Retsch) at 500 rpm for 20 minutes. Two coatings were applied from each slurry on AI foils to create electrodes with sulfur loadings of approximately 2 and 4 mg/cm². NMPbased electrodes were dried in an oven at 60 °C, and water-based electrodes were dried at 30 °C. The subsequent step involved assembling standard 2025 coin cells for electrochemical tests. Initially, 12.6 mm electrode punches were made from the sulfur electrodes and transferred into a glovebox with oxygen and water content maintained below 1 ppm. The battery cells were assembled using a Li foil anode, Celgard 2400 separator, and DOL:DME 1:1, 1M LiTFSI, 1 wt.% LiNO₃ electrolyte, with the electrolyte-to-sulfur ratio of 20 μ L/mg. Following cell assembly, the cells were connected to the battery tester (Neware BTS4000) and allowed to rest for 12 hours. The next step involved galvanostatic cycling of Li-S cells for 20 cycles at a discharge-charge rate of 0.1 C (1C = 1.675 mA/g-sulfur) in the voltage range of 1.6-2.8 V.

4.2. SEM characterization

Small pieces (approximately 0.5 cm²) of electrodes were cut with a sharp knife for both surface and cross-section imaging. To attach sample electrodes to the standard SEM pin stubs silver glue was used and the samples were investigated with no additional conductive coat. As sulfur is known for

its sublimation at room temperature in high vacuum ⁵⁸ the FEI Quanta 250 was used in environmental mode for scanning electron microscopy (ESEM). In this method, a gaseous secondary electron detector (GSED; 200-2600 Pa pressure range) was used which collects electrons emitted through the low vacuum. In this work, we used 1150 Pa air pressure to reach the optimum signal-to-noise ratio at 30kV.

4.3. X-ray micro-computed tomography

X-ray micro-CT was performed on the sulfur electrode mounted onto a stainless steel pin with quick setting epoxy. A lab-based micro-CT instrument (Zeiss Xradia Versa 620, Carl Zeiss Inc.) was used, containing a polychromatic micro-focus sealed source set to an accelerating voltage of 60 kV on a tungsten target at a maximum power of 6.5W. The scintillator was coupled to a 20X objective lens and 2048 x 2048 pixel CCD detector with a pixel binning of 1. The source-sample distance was set to 32 mm and the sample-detector distance set to 13.7 mm, resulting in a pixel size of 375 nm and field of view of ca. 0.72 mm. There was no significant geometric magnification as the sample was set close to the detector to reduce the effects of penumbra blurring arising from the cone beam nature of the source. The sample was rotated through 360° with radiographs collected at discrete angular intervals amounting to a total of 1601 projections. The radiographic projections were then reconstructed with proprietary reconstruction software (XMReconstructor, Carl Zeiss Inc.) using a modified Feldkamp–David–Kress (FDK) algorithm for cone beam geometry.

4.4. Image post-processing, segmentation and analysis

The micro-CT dataset was imported into Avizo (Thermo Fisher). An edge-preserving de-noising non-local means filter was applied (spatial standard deviation 5, Intensity standard deviation 0.2, search window 10 px, local neighborhood 3 px). A mixture of manual labelling (using contrast thresholding) and a watershed segmentation algorithm were used to segment the volume into five phases, corresponding to the sulfur, aluminum foil current collector, carbon-binder domain (CBD), exterior, and internal pore voids in descending order of X-ray attenuation contrast. The binarized sulfur and internal pore voids were each separated into discrete particles for particle size distribution analysis using a random-walk distance (RWD) based algorithm. The RWD map was calculated for each subvolume, and the regions corresponding to separate particles identified

using a H-Extrema watershed algorithm. The corresponding regions were overlaid on the binarized volumes to label the voxels within separated regions as individual particles. Morphological parameters including the particle volume were obtained via voxel counting in Avizo.

4.5. Zeta potential measurement

Malvern Zetasizer was employed to characterize the surface charge of carbon, sulfur and their mixture within the water-based dispersions, containing CMC-SBR and LiPAA binders. The dispersion, were prepared with the identical formulation and mixing conditions as the electrode slurries. Afterwards, approximately 10 microliters of dispersion were withdrawn and then diluted at a 1:200 ratio. The zeta potential in each dispersion was determined after adjusting the pH value in the range of 3 to 12 using aqueous 0.1N hydrochloric acid and 0.1M sodium hydroxide solutions.

4.6. Contact resistance and tortuosity measurement

Swagelok-type cells made of PFA (inner diameter 12.7 mm) were used with stainless steel bars as current collectors and a stainless steel compression spring to establish consistent and reproducible contacts. The assembly comprised two identical sulfur electrodes, separated by two glass fiber separators (Whatman GF/C, 250 µm, 90% porosity) and 500 microliter of DOL:DME 1:1, 1M LiTFSI, 1 wt.% LiNO₃ electrolyte. The electrodes thickness was measured by a Mitutoya micrometer with 0.1 microns accuracy, and the porosity was calculated according to the known values of thickness, particle density and formulation. Electrochemical impedance spectroscopy (EIS) analysis was conducted using a Biologic VMP3 potentiostat, applying a perturbation voltage of 10mV across a frequency range of 10 mHz to 1 MHz. The experimental data was then fitted by Zview software.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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