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Coupling of S@aerogel and Si/SiO_x Nanospheres Electrodes with "Polysulfide" Salt-Free Electrolytes in a Fluorine-Free Lithium-Ion Batteries

Marco Agostini,* Jang-Yeon Hwang,* Piotr Jankowski, Hyeona Park, Chaiwon Lee, Hansu Kim, Shizhao Xiong, Carmen Cavallo, Arcangelo Celeste, Sang-Gil Woo, Jinhua Sun, Sergio Brutti, Yang-Kook Sun,* and Aleksandar Matic

Li-ion batteries play a pivotal role in powering electric vehicles and storing renewable energy. To enable their widespread adoption, it is imperative to explore new materials that reduce costs and enhance energy density. Sulfur and silicon exhibit promising characteristics as cathodes and anodes, respectively, and perform well in Li half-cells. However, their effective coupling in Li-ion configurations presents challenges. A major hurdle lies in identifying an electrolyte that ensures stable interphases and prolonged cycling while prioritizing safety and cost-effectiveness. This study introduces a groundbreaking approach by customizing a "salt-free" electrolyte solution compatible with both Li/sulfur and Li/silicon cells. The innovation involves dissolving lithium polysulfide in a diglyme solvent to facilitate Li-ion transfer. This improves cell safety due to the low flammability of the solvent and the absence of fluorine, while also ensuring faster Li-ion transport and prolonged stability of the solid electrolyte interphase. By integrating this tailored electrolyte with engineered electrodes, including a free-standing reduced graphene oxide aerogel with \approx 74% sulfur and high areal capacity Si/SiO_x nanospheres, a unique "salt-free" Li-ion battery configuration is demonstrated. The findings present a promising avenue for developing costeffective, safe, high-performance lithium-ion batteries.

1. Introduction

The quest for novel materials with enhanced performance is pivotal in establishing lithium-ion batteries (LiBs) as contenders for propelling electric vehicles (EVs) and storing renewable energy.^[1] Beyond the imperative to increase the power and energy densities, the reduction of LiB costs is equally crucial. Currently, commercial LiBs rely on cathodes featuring nonabundant and expensive elements such as Ni and Co, whereas the anode is graphitebased.^[2,3] Both electrodes operate on lithium-ion intercalation chemistry, prompting recent advances in developing electrodes that surpass the traditional "intercalation" energy limit through a "conversion" reaction with Li-ions.^[4,5] Among the array of materials proposed by the LiB scientific community, S cathodes, and Si anodes have emerged as promising candidates for achieving high energy densities with significant

M. Agostini, S. Xiong, A. Matic Department of Physics Chalmers University of Technology SE41296 Göteborg, Sweden E-mail: marco.agostini@uniroma1.it

M. Agostini Department of Chemistry and Drug Technologies Sapienza University of Rome P.le Aldo Moro 5, 00185 Rome, Italy

J.-Y. Hwang, H. Park, C. Lee, H. Kim, Y.-K. Sun Department of Energy Engineering Hanyang University Seoul 04763, South Korea E-mail: jangyeonhw@hanyang.ac.kr; yksun@hanyang.ac.kr

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/sstr.202500096.

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J.-Y. Hwang, H. Kim, Y.-K. Sun Department of Battery Engineering Hanyang University Seoul 04763, South Korea

P. Jankowski Faculty of Chemistry Warsaw University of Technology plac Politechniki 1, 00-661 Warsaw, Poland

C. Cavallo Centre for Materials Science and Nanotechnology Department of Chemistry Oslo University 0371 Oslo, Norway

A. Celeste, S. Brutti Department of Chemistry Sapienza University of Rome P.le Aldo Moro 5, 00185 Rome, Italy

S.-G. Woo Advanced Batteries Research Center Korea Electronics Technology Institute 25 Saenari-ro, Bundang-gu, Seongnam, Gyeonggi 13509, Republic of Korea SCIENCE NEWS _____

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cost reduction.^[6] Notably, both S and Si offer economic advantages over $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (NMC) and graphite.

Si, the second most abundant element in the Earth's crust (\approx 28%), is widely utilized in the electronics market, whereas S is a nontoxic coproduct of the petroleum industry.^[7,8] Over the past decade, S has garnered considerable attention as a cathode material for Li, leveraging a conversion reaction to form Li2S compounds and reverting to $S_{8.}^{[8]}$ Despite having a five times higher theoretical energy density than NMC-based electrodes, the widespread adoption of sulfur electrodes faces hurdles, primarily owing to the low electronic conductivity of S, $\approx 10^{-30}$ S cm⁻¹. Second, to the formation of intermediate products during the Li-ion reactions, particularly lithium polysulfides (LiPs).^[9] These species exhibit high solubility in the electrolyte medium, especially when featuring long polysulfide chains, leading to their migration to the anode and partially back to the cathode, resulting in the so called "shuttle effect".^[10] This mechanism results in the depletion of the active material during Li/S battery operation, reducing the cycle life. Numerous studies have attempted to address these challenges by confining S to carbon-based structures.^[11] While carbon-based structures effectively enhance the electronic conductivity of electrode in LiBs, their nonpolar surfaces and internal sulfur confinement restrict active material utilization to a small fraction.^[12] Free-standing structures with hydrophilic surfaces have been proposed to retain lithium polysulfides (LiPs) on the cathode side. This approach, which avoids using inert components such as polymer binders and current collectors, maximizes active material utilization.^[13]

Similar to S, Si has gained attention as an anodic material in LiBs owing to its low average (de)-lithiation potential and high gravimetric and volumetric capacities. However, it faces challenges in reacting with Li ions.^[14-16] Volume changes during the conversion to Li_xSi_y result in Si structure expansion, causing particle fractures, and loss of electrical contact.^[17,18] Various engineering approaches have been proposed, including producing composites with carbon hosts to tailor the dimensions of the Si particles, porosity, and void space,^[19] or introducing polymeric binders with high elasticity to prevent the Si anode from cracking upon expansion during the (de)-lithiation phases.^[20] Although S and Si electrodes individually excel in Li half-cells, their coupling in Li-ion configurations is complex.^[21-23] Balancing is not a significant issue, owing to their comparable specific capacities.^[8,16] However, finding an efficient and cost-effective electrolyte that ensures stable electrode interphases and facilitates long-term cycling remains challenging.^[24,25]

Here, we propose a novel approach: the utilization of a specifically formulated "salt-free" electrolyte solution to couple sulfur and silicon electrodes efficiently. This innovative solution consists of dissolved lithium polysulfide (Li_2S_8) in diethylene glycol dimethyl ether (DEGDME, G2) solvent. The resulting electrolyte ensures rapid Li-ion transport, prolonged stability of the solid electrolyte interphase, and enhanced safety compared with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI)-containing

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solutions. Combining this electrolyte with engineered freestanding reduced graphene oxide aerogel containing \approx 74% S and high areal capacity Si/SiO_x nanosphere anodes, we demonstrate a unique "salt-free" LiB configuration with extended cyclelife, reduced cost, and enhanced safety. In particular, we designed a complete fluorine-free Li-ion battery configuration, very important to avoid formation of perfluorinated alkylated substances (PFAS) during battery operation.

2. Results and Discussion

A meaningful evaluation of the relevant merit of any electrolyte formulation requires considering criteria such as cost, safety, Li-ion transport properties, and solid electrolyte interphase (SEI) stability. The cost of the electrolyte solution is primarily affected by the Li salt dissolved in the solvent. The reduction in cost of Li2S8 polysulfide synthesis respect to LiTFSI is of -200 kg⁻¹, calculated considering the cost kg⁻¹ of raw materials used to synthesized it, as illustrated in Figure 1a-left. Turning to safety, the flammability of any liquid electrolyte is driven by the flash point of the solvent. Here, we compared the selected organic solvent (DEGDME) with a standard solvent, dioxolane/dimethoxyethane (DOL/DME) (1:1 volume ratio), which is commonly used for Li/S battery electrolyte synthesis. The flash point (T_{flash}), representing the lowest ignition temperature of a solvent vapor, is a key parameter for assessing flammability.^[26,27] The DEGDME solution exhibited a significantly higher T_{flash} (55 °C) compared to the DOL/DME solution (T_{flash} of 12 °C), indicating improved safety (Figure 1a-center). Consequently, DEGDME was selected as the solvent for this study.

Two electrolytes were compared: 1) LiTFSI (0.5 M) in DEGDME and 2) 0.5 M Li₂S₈/DEGDME solution. This last formulation was prepared by mixing 1 mol of Li and 4 mol of S in 1 L of DEGDME. Both electrolytes were characterized in terms of their Li-ion diffusion coefficient, as shown in Figure 1c–right. The Li₂S₈ solution exhibits a Li transference number of 0.5, whereas the LiTFSI solution shows a lower value of 0.36. This difference is further discussed in the context of molecular dynamics (MD) calculations (**Figure 2**).

The ionic conductivities of the electrolytic solutions were assessed at various temperatures and are shown as Arrhenius plots in Figure 1b. Both solutions demonstrated similar values, falling within the range 10^{-2} to 10^{-3} S cm⁻¹, between 70 and 8 °C. This outcome suggests that Li polysulfide can ensure conductivity slightly lower to that of commercial lithium salts, as the higher viscosity of the solution, with only minimal reduction likely compensated greater Li transference. Li plating-stripping tests were conducted to evaluate the stability of the electrolytic solutions, Figure 1c. The enhanced stability of the Li₂S₈-solution is attributed to its low overpotential of $\approx 10 \text{ mV}$ (green line), which is similar to that of LiTFSI. In the extended tests, the Li₂S₈-solution demonstrated notable stability, showing no signs of Li dendrite formation. Conversely, the LiTFSI-added electrolyte resulted in an increased overvoltage over time, indicating Li dendrite formation and a less stable SEI layer.^[28] The enhanced stability of the Li₂S₈ solution can be attributed to two factors. First, the Li stripping/plating reaction occurs at \approx 0 V, which is considerably different from the polysulfide

Department of Industrial and Materials Science Chalmers University of Technology SE41296 Göteborg, Sweden

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Figure 1. Characteristics of the electrolyte solutions. a) Cost comparison of LiTFSI-salt and Li_2S_8 polysulfide (left). Flash point comparison between DOL/ DME and DEGDME solvents (center). Li⁺ transference number calculated from the MD modeling for DEGDME LiTFSI 0.5 M and DEGDME Li₂S₈ 0.5 M and b) Arrhenius plot of conductivities. c) Cycling stability Li/Li symmetrical cells using the above electrolytes.



Figure 2. Electrolyte properties: MD simulations. Snapshots of MD simulations with cationic (blue) and anionic (red) clusters of a) 0.5 M Li_2S_8 and b) LiTFSI in G2 solvent. Corresponding radial distribution functions with coordination numbers for c) 0.5 M Li_2S_8 and d) LiTFSI. e) Comparison of the Raman spectra of LiNO₃ 0.4 M in DEGDME (blue line), LiTFSI 0.5 M in DEGDME (red line), LiTFSI 0.5 M LiNO₃ 0.4 M in DEGDME (green line), and the solvent DEGDME (black line). f) Comparison of the Raman spectra of Li₂S₈ 0.5 M in DEGDME (blue line), Li₂S₈ 0.5 M LiNO₃ 0.4 M in DEGDME (plack line).

oxidation/reduction, typically between 1.8 and 2.6 V versus Li^+/Li . This difference ensured that the stability of the SEI layer was unaffected. Second, the SEI layer formed by the

decomposition of polysulfide is less resistive, facilitating the stripping/plating of Li without dendrite formation.^[29] In particular, Li_2S_8 polysulfide salt was revealed to be the most stable

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among various long-chain polysulfides, and the more performing in terms of SEI stability when used in Li/S cells.^[28,29]

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MD simulations were performed to analyze the solvation structure of ions in the two electrolytes as well as the ion conduction mechanism (Figure 2). In the G2-based electrolyte with the standard LiTFSI salt, Li+ ions are strongly coordinated by ether oxygen on the glyme, in line with an almost complete separation of anions from cations. In the 0.5 M LiTFSI electrolyte, two charged strongly-bonded cluster/specie were distinguishable within the electrolyte: (LiG2₂)⁺ and TFSI⁻. Thus, lithium transport across this formulation is driven by the mobility of the entire $(LiG2_2)^+$ solvated cluster (Figure 2b) whereas negative charge transport is easier thank to the almost absent solvation shell around the TFSI⁻ anion. This behavior is common in diluted systems where the coordination of lithium is dominated by solvent's molecules.^[30,31] This description matches the relative values of the transport number that is dominated by the anionic component. Conversely, in the 0.5 M Li₂S₈-based electrolyte, the lithium coordination environment is more complex also including the S_8^{2-} specie. The majority of lithium ions solvation is described by different clusters: one Li₂S₈, one cationic $-(\text{LiG2}_2)^+$, and one anionic $-(\text{LiS}_8)^-$, Figure 2a. In fact, simulations predicted a partial dissociation of the Li2S8 salt, thus resulting in the inevitable strong binding between each anion and at least one lithium cation (Figure 2c). The mobility of the neutral or the anionic clusters are stiffer compared to the naked TFSI⁻ anion (Figure 2d), resulting in a larger calculated transference number of cations (0.50 and 0.36 for 0.5 M Li₂S₈ and 0.5 M LiTFSI, respectively). Diffusion coefficients of all molecules and ions obtained from MD simulation are reported in Table S1, Supporting Information (SI) section. Raman spectroscopy has been used to check the various components solvation in the liquid phase as well as verify the speciation of polysulfides. Besides the solvent, i.e., DEGDME, five formulations have been analyzed: (1) LiNO₃ 0.4 M in DEGDME, (2) LiTFSI 0.5 M in DEGDME, (3) LITFSI 0.5 M LINO₃ 0.4 M in DEGDME, (4) Li_2S_8 0.5 M in DEGDME, and (5) Li_2S_8 0.5 M LiNO₃ 0.4 M in DEGDME, see Figure 2e,f. As expected, the Raman spectra of the formulations (1), (2), and (3) nicely highlight the vibrational fingerprints^[32,33] in the solutions of uncoordinated and coordinated ions: (i) 741 cm⁻¹ Li⁺TFSI⁻ solvated ion pair overlapped with TFSI⁻ free anion, (ii) 881 cm⁻¹ Li⁺DEGDME charged pair, (iii) 1241 cm⁻¹ Li⁺TFSI⁻ solvated ion pair overlapped with $TFSI^{-}$ free anion, (iv) 1037 cm⁻¹ Li⁺NO₃⁻ solvated ion pair overlapped with NO_3^- free anion, and (v) $1050 \text{ cm}^{-1} \text{ Li}^+\text{DEGDME}$ charged pair, see Figure 2e. The comparison of the Raman spectra of formulations (4) Li_2S_8 0.5 M in DEGDME, (5) Li_2S_8 0.5 M LiNO₃ 0.4 M in DEGDME and the solvent DEGDME is shown in the Figure 2f. The spectra of formulations (4) and (5) are dominated by the polysulfides/sulfides-related peaks in the 200–600 cm^{-1} range with additional features at about 750–900 and $1050-1070 \text{ cm}^{-1}$. More in details, according to the recent literature, the overlapped peaks at (vi) 380, (vii) 443, (viii) 512, and (ix) 535 cm^{-1} are likely assigned to the vibrational fingerprints^[30,32-34] of (vi) S_8^{2-} , S_7^{-} , S_7^{2-} , Li₂S, LiS⁻, or S²⁻, (vii) S_6^{2-} , S_4^{-} , S_3^{2-} , or S_4^{2-} , (viii) S_4^{-} or S_7^{-} (ix) S_3^{-} , whereas the peaks above 700 cm^{-1} are likely related to the presence of (x) $809 \text{ cm}^{-1} \text{ S}_{x}^{-}$ and (xi) 1065 cm $^{-1} \text{ S}_{2}\text{O}_{4}^{2-}$. The lack of peaks below 250 cm⁻¹ suggests the absence in the electrolyte

www.small-structures.com formulation of undissociated Li₂S₈ or S₈ rings.^[34–36] However, the experimental data suggest clearly that the Li₂S₈ species undergoes to a spontaneous disproportion in the electrolyte possibly originating a number of shorter solvated polysulfides and S₂O₄^{2–} thanks to the reactivity toward the oxygen atoms of the ethereal solvent DEGDME. Overall, the structure of the DEGDME Li₂S₈-based electrolytes has a very complex solvation landscape due to the occurrence of disproportion reactions and irreversible reactivity toward the ethereal solvent.^[29,37,38] Therefore, the comparison to the MD is based by the nature of the computational simulations that do not consider the chemical reactivity. The partial dissociation of polysulfides highlighted in the Raman spectra agrees with the finding of MDs where the formation of LiS₈⁻ has been observed.

Three-dimensional structures such as those based on graphene aerogels with abundant oxygen sites can enhance the binding between the carbon surface and lithium polysulfides, ensuring higher efficiencies for the electrocatalytic reaction between Li and S.^[39–42] The synthesis of the S electrode, as shown in **Figure 3**a, commenced with a reaction between Li₂S and elemental S, as follows:

$$\operatorname{Li}_{2}S + \frac{n-1}{8}S_{8} \xrightarrow{\sim 6h} \operatorname{Li}_{2}S_{n} \tag{1}$$

A homogeneous graphene oxide (GO) aqueous solution was sonicated until the GO sheet aggregates were reduced and then mixed with the polysulfide solution in a ratio of 2.5:1 v/v. The chemical reduction process employs a mild reducing agent, L-ascorbic acid, to restore the sp² network, along with HCl as a catalyst. The final solution underwent dilution with distilled water, sonication for homogeneity, and reduction at 90 °C, a very low and safe temperature. The resulting hydrogel was carefully extracted, dried using antistatic wipes, and frozen in a closed container containing liquid nitrogen. Subsequently, the quenched hydrogel was transferred to a freeze dryer to remove water while preserving high porosity, resulting to S@rGO aerogel with a 3D structure, as shown in the scanning electron microscopy (SEM) image in the inset Figure 3a. The transmission electron microscopy energy-dispersive spectroscopy (TEM-EDS) image in Figure 3b shows that S particles (yellow) are dispersed throughout the carbon aerogel matrix (green) and oxygen functional groups (orange). The reported synthetic method has been conceived to design a 3D carbon with high porosity to host sulfur loading of 74% (see thermogravimetric analysis in Figure S1, Supporting Information section) with a final surface area of \approx 35 m² g⁻¹, as calculated from absorption/desorption isotherms of Figure 3c, using Brunauer-Emmett-Teller analysis, which is much lower than that of the pristine aerogel ($1000 \text{ m}^2 \text{ g}^{-1}$), indicating that sulfur was distributed in the flakes of the reduced graphene oxide (rGO) aerogel. Considering the isolating nature of elemental sulfur, 10^{-30} S cm⁻¹, reaching high loading in S-based electrodic materials is not common in the state-of-art, in particular when maintaining good cycling performance. Structural features of the S@rGO aerogel were examined through XRD analysis, see Figure 3d. All characteristic sulfur peaks were observed (S₈, JCPDS#850799)^[43] and superimposed on the expected broad peak of rGO centered at 24°,^[42] matching the calculated S₈ diffractogram. A significant disorder of the graphene



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Figure 3. Synthetic pathway of S@rGO aerogel and physical-chemical characteristics. a) Schematic of 3D S@rGO aerogel network architecture and related morphology from SEM image. b) TEM images and corresponding EDS mapping for C (green), S (yellow), and O (orange). c) Nitrogen adsorption/ desorption isotherms. d) XRD pattern with experimental and calculated results. e) Raman spectrum measured at 532 nm laser excitation wavelength.

layers was revealed by Raman spectroscopy analysis (Figure 3e), as is evident from the I(D)/I(G) intensity ratio (\approx 2.2), indicating the presence of structural defects in the rGO structure.^[44]

To support the hypothesis that the presence of oxygencontaining functional groups leads to stronger polar-polar interactions between the carbon host and lithium polysulfide, we evaluated the binding energies (BEs) of S and LiPs toward graphene and rGO by using the density functional theory (DFT), as shown in Figure 4a. The carbon surface was modeled with a $C_{54}H_{20}$ for graphene and $C_{55}H_{18}O_8$ for rGO; the details of the bonding motifs, methods, and models are presented in the Experimental paragraph reported in Supporting Information section. We systematically investigated the various chemical species present in Li/S cells during charging/discharging from S₈ to different Li_2S_n with $1 \le n \le 8$. Computational DFT data demonstrated that the presence of oxygen in the graphene layer fostered stronger interactions with all LiPs, resulting in higher binding energies (Bes). This effect, originated by the larger electronegativity of oxygen compared to carbon, leads to a hindering of the dissolution of LiPs ion from the surface of graphene layers where oxygen moieties are present in comparison with the strongly hydrophobic graphene honeycomb surface. Subsequently, galvanostatic cycling tests were conducted using S@rGO as the cathode and Li₂S₈/LiNO₃ in DEGDME as the electrolyte (Figure 4b). At this stage, LiNO₃ additive was introduced into the electrolytic solution to mitigate the "shuttle" effect of LiPs on the Li surface.^[45,46] Notably, this additive was excluded from the electrolyte in the complete Li-ion cell configuration.

The cell was cycled at different sulfur loadings, starting from 5 mg cm^{-2} , $50 \mu \text{m}$ thickness, and employing a current rate of C/10 (1 C = 1675 mA g⁻¹). The voltage profile at the 20th cycle in Figure 4c shows the typical discharge/charge curve of Li/S cell, while prolonged cycling (Figure 4d) demonstrates a stable and reversible capacity of 600 mAh g^{-1} . The cycling of electrodes at various S loadings revealed that increasing the mass loading did not strongly affect the Li/S cell stability (Figure 4e). S@rGO electrode performance were further evaluated in 0.5 M LiTFSI, 0.4 M LiNO₃ DEGDME electrolyte, Figure S2, Supporting Information section. Both cycling tests show similar performance, including capacity decay in the first 10 cycles, as sulfur not confined in the pores of the aerogel tend to solubilize in the electrolyte, buffering further dissolution of active material, while the voltage profiles result different, as the Li₂S₈ polysulfide salt reduces the average discharge overpotential and furthermore participates to the electrochemical reaction. As the percentage of the Li₂S₈ to the overall reaction is difficult to calculate, the mass of sulfur deriving from its presence is not considered in the overall specific capacity of the Li/S cell. This consideration is necessary to have a real comparison of all Li/S cells reported in this work, as both LiPs and LiTFSI electrolytes are used with the same volume. Rate capabilities test of the S@rGO electrodes was performed, Figure S2, Supporting Information section. The figure shows that the Li/S@rGO cell recovers about 100% of the capacity at cycle 5th after lowering back the current to C/20, while increasing the current rate the cell still delivers good capacity at C/5 (about 500 mAh g^{-1}) and at C/3 (350 mAh g^{-1}).



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Figure 4. Binding energies and electrochemical properties of S@rGO in Li-half cell configuration. a) Strengths of interaction between different LiPs species and rGO substrate. b) Schematic of Li-half cell configuration using S@rGO aerogel. c) Voltage profile and d) cycling performance of 5 mg cm⁻² sulfur loading S@rGO cathode in half-cell. e) Cycling performance of aerogel at different areal sulfur loadings. Current rate C/10 (1 C = 1675 mA g⁻¹); cell configuration Li/DEGDME Li₂S₈ 0.5 M, LiNO₃ 0.4 M/S@rGO.



Figure 5. Performance of Li-ion cell built using S@rGO cathode, Si/SiO_x anode, and "salt" free electrolyte. Schematic of Li/half-cells for a) S@rGo and b) Si/SiO_x electrodes. c) Balance in areal capacity between anode and cathode. d) Voltage profiles at different cycles (see in inset) and e) prolonged S@rGO-Si/SiO_x cell stability. Current rate C/10 ($1 C = 1675 \text{ mA g}^{-1}$), voltage cut-off 0.8–2.6 V.

Normally, high-loading sulfur-based electrodes using carbon hosts show scarce performance at high current rates, differently our S@rGO thanks to the presence of reduced graphene oxide, which has a good electrical conductivity allows for good performance even at C/3, see Figure S3, Supporting Information section.^[47,48] To construct a practical Li-ion cell,



we selected the aerogel electrode delivering a stable areal capacity of 3 mAh cm^{-2} (Figure 5a). This electrode was then coupled with a Si/SiO_x nanosphere anode delivering \approx 3.5 mAh cm⁻² (Figure 5b), resulting in a negative to positive ratio (N/P) of 1.2 (Figure 5c). The Si/SiO_x nanosphere electrode is characterized by high performance in terms of both capacity and cycle life.^[23] The material has a well-defined spherical morphology with a size of 200 nm, consisting of nonstoichiometric silicon oxide (SiO_x) , with crystals of about 5 nm in size on the surface of the nanosphere, see Figure S4, Supporting Information section. This electrode was tested in Li-half cell using Li₂S₈ 0.5 M/DEGDME electrolyte. The current rate selected was the same of the cell Li/S@rGO of Figure 4c (0.1 C = 167.5 mA g^{-1}). The material delivered a stable capacity of $600 \text{ mAh} \text{ g}^{-1}$, even at active material loading of about 5.8 mg cm^{-2} , with an average working voltage of 0.3 V versus Li, furthermore showing a good rate capability performance, see Figure S5, Supporting Information section. Previously to be used in full Li-ion cell configuration, the Si/SiO_x electrode is fully lithiated by direct contact with Li-metal foil using LiTFSI 0.5 M DEGDME electrolyte.^[49] The voltage profiles reported in Figure 5d showed a characteristic shape resulting from coupling the two electrodes. The prolonged cycling stability revealed an initial capacity of 750 mAh g⁻¹, slightly decreasing to 600 mAh g^{-1} at the 200th cycle and stabilizing at $\approx 500 \text{ mAh g}^{-1}$ at the cycle 600th.

3. Conclusion

In conclusion, our study highlights the significant advantages of eliminating fluorine-based Li salt from an electrolyte solution and strategically replacing it with a polysulfide-based alternative. This substitution not only improves the Li/interphase interactions, leading to reduced overvoltage and mitigated Li-dendrite formation, but also results in a substantial reduction in electrolyte manufacturing costs. The calculated cost reduction, coupled with enhanced safety through a low-flammability solvent and fluorine-free salt, renders this approach a promising avenue for a more cost-effective and secure LiB technology. Moreover, our electrolyte design demonstrated versatility, proving to be suitable for both S@aerogel and Si/SiOx electrodes in Li half-cell configurations. The presence of polysulfides in the electrolyte solution was instrumental in enhancing the performance of Li-ion cell based on self-standing S@aerogel and Si/SiO_x electrodes, showing stable cycling performance even at a high areal capacity ranging between 3 and 2 mAh cm^{-2} for over 600 cycles. The scalability and compatibility of this "salt-free" LiB configuration are promising for large-scale applications. The successful combination of this electrolyte with engineered electrodes such as free-standing rGO aerogels containing \approx 74% sulfur and high areal capacity Si/SiO_x nanospheres is a crucial step toward realizing a unique and practical solution for advanced energy storage systems. So far, compared to state-of-art Li-ion cell designed using sulfur-based electrodes, this work reports the best performance, see Figure S6 and Table S2, Supporting Information section. $^{\left[23,50-55\right] }$ Further optimization and exploration of this innovative configuration could pave the way for next-generation LiBs with improved efficiency, reduced costs, and enhanced

safety, thus addressing key challenges in the field of energy storage technology.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Marco Agostini: conceptualization (lead); methodology (lead); writing original draft (lead); writing—review & editing (lead). Jang-Yeon Hwang: supervision (equal); writing—review & editing (equal). Piotr Jankowski: investigation (equal). Hyeona Park: investigation (equal). Chaiwon Lee: validation (equal). Hansu Kim: methodology (equal). Shizhao Xiong: data curation (equal); formal analysis (equal). Carmen Cavallo: investigation (equal). Arcangelo Celeste: investigation (equal). Sang-Gil Woo: investigation (equal). Jinhua Sun: investigation (equal). Sergio Brutti: supervision (equal); writing—review & editing (equal). Yang-Kook Sun: writing—review & editing (equal). Aleksandar Matic: funding acquisition (equal); supervision (equal); writing—review & editing (equal).

Data Availability Statement

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

Keywords

fluorine-free lithium-ion batteries, "salt-free" electrolyte, solid electrolyte interphase stability, sulfur/silicon electrodes

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