Nano-Confinement of Insulating Sulfur in the Cathode Composite of All-Solid-State Li–S Batteries Using Flexible Carbon Materials with Large Pore Volumes

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ABSTRACT: Durable nanostructured cathode materials for efficient all-solid-state Li–S batteries were prepared using a conductive single-walled 3D graphene with a large pore volume as the cathode support material. At high loadings of the active material (50–60 wt %), microscale phase segregation was observed with a conventional cathode support material during the charging/discharging processes but this was suppressed by the confinement of insulating sulfur into the mesopores of the elastic and flexible nanoporous graphene with a large pore volume of 5.3 mL g⁻¹. As such, durable three-phase contact was achieved among the solid electrolyte, insulating sulfur, and the electrically conductive carbon. Consequently, the electrochemical performances of the assembled all-solid-state batteries were significantly improved and feasible under the harsh conditions of operation at 353 K, and improved cycling stability as well as the highest specific capacity of 716 mA h per gram of cathode (4.6 mA h cm⁻², 0.2 C) was achieved with high sulfur loading (50 wt %).

KEYWORDS: nanoporous carbon, 3D graphene, lithium-sulfur battery, all-solid-state battery, large pore volume

1. INTRODUCTION

The holy grail of practical application for the given secondary batteries is to employ inexpensive active materials that can be used at as much loading as possible while providing highly durable discharge/charge cycles with the full utilization of energy stored. The use of lithium metal as an anode material of secondary batteries is an attractive means to achieve a high density storage of energy because of its high gravimetric theoretical capacity (3861 mA h g^{-1}) and low electrochemical potential of -3.0 V versus a normal hydrogen electrode.¹⁻⁸ On the contrary, various compounds, such as $LiCoO_2$,⁸⁻¹¹ LiFePO₄,¹²⁻¹⁴ Mo₂S,¹⁵ Si,^{16,17} and S,¹⁸⁻²⁸ have been investigated as the active materials of the counterpart cathodic reactions. Among them, Li-S systems with sulfur as a cathode material are promising because sulfur is inexpensive, abundant, and readily available. Moreover, Li-S systems enjoy a high theoretical capacity of 1672 mA h per gram of sulfur with a cathodic reaction of $2Li^+ + S + 2e^- \rightleftharpoons Li_2S$ because of the light

atomic weight of S, and this will be beneficial to high energy density of secondary batteries that is required for improving the mileage of electric vehicles (EVs). However, poor durability remains a problem,²⁹ and the safety issues that come from the use of volatile organic solvents in the liquid electrolyte has yet to be solved.

A promising strategy to solve the abovementioned problems is to realize an all-solid-state configuration, $^{30-48}$ which uses solid-state-electrolytes for the conveyance of the lithium ion during the charging and discharging processes. $^{10,30-47,49,50}$

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However, sulfur itself has poor electrical conductivity (5 \times 10^{-30} S cm⁻¹),⁴³ and this limits the efficient utilization of S. In addition, sulfur expands by up to 179% of its original volume upon lithiation. Therefore, S has to be supported on electrically conductive materials with mechanical toughness/flexibility to retain the conductive paths as volume changes. To date, light carbon materials, such as reduced graphene oxides (rGOs),⁵¹ carbon nanotubes,^{44,52–54} polyvinylpyrrolidone (PVP)-derived carbons,⁵⁵ and activated carbons,^{35–37,56,57} have been examined as conductive supports. However, the small pore volume limits sulfur loading to below 50 wt %, and the resulting total capacities are insufficient for practical applications. The nanoporosity of conductive materials is usually a trade-off with electrical conductivity and mechanical toughness, and the development of next-generation support materials has been a challenge to fulfill the seemingly incompatible requirements of high porosity, high electrical conductivity, and excellent mechanical properties.

We have recently developed an unprecedented nanoporous graphene (NPG), 5^{8-61} consisting mostly of single-layered graphene walls. NPG was prepared by using alumina nanoparticles as a hard template. Notably, NPG has a large pore volume (2.79 cm³ g⁻¹), high electrical conductivity (up to 18 S cm⁻¹),⁵⁹ and a carbon framework that is mechanically tough and flexible with a bulk modulus of 0.79 GPa,⁵⁸ thus enabling reversible shape compression/recovery at large strains (88%). Additionally, the electrochemical stability of NPG is extremely high because the amount of reactive edge sites in the high-quality graphene framework is low.⁵⁹ All these extraordinary properties distinguish NPG from other carbon materials, 35-37,44,51-57,62-65 and this fact makes NPG an interesting candidate as a sulfur support in Li-S batteries. Meanwhile, the nanostructure of NPG can be well tailored to meet the requirements of specific applications. The previously reported NPG had a mean mesopore size of 5.8 nm, whereas the new NPG developed in this study has larger mesopores (10 nm) and an extremely large nanopore volume $(5.3 \text{ cm}^3 \text{ g}^{-1})$ to accommodate a large amount of sulfur. The effects of crystallinity on battery performance were investigated by preparing two types of NPGs with different annealing temperatures. Activated carbon (MSC30) was reported to facilitate the best battery performance,^{35,48} and we confirmed that MSC30 indeed gave a charge/discharge capacity approaching theoretical maxima at room temperature at a slow rate. Therefore, MSC30 was used as the reference material. The materials before and after S loading were fully characterized by X-ray diffraction (XRD), field emissionscanning electron microscopy (FE-SEM), high-resolution transmission electron microscopy (HRTEM), N₂ physisorption, Raman spectroscopy, conductivity measurements, stressstrain testing, and highly sensitive temperature-programmed desorption (TPD) measurements.^{66,67} Moreover, the effects of the carbon supports on battery performance and cyclability were examined with respect to the nano-confinement effect⁶ of the elastic carbon material by charge/discharge tests and post analyses after charge/discharge by high-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) coupled with energy-dispersive X-ray spectroscopy (EDS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS).

2. EXPERIMENTAL SECTION

2.1. General. All the chemicals were reagent grade, purchased commercially, and used without further purification unless otherwise noted. Li₁₀GeP₂S₁₂ (LGPS)¹⁰ was purchased from MTI Corp. Li₃PS₄ (LPS) was purchased from NEI Corp. Sulfur (99.99%) was supplied by Tsurumi Chemical Industry Co., Ltd. Activated carbon (Maxsorb MSC30) was supplied by Kansai Coke and Chemicals Co., Ltd. Li foil (20 mm × 30 m, 0.2 mm thickness) was supplied from Honjo Metal Co., Ltd. In foil (100 mm × 100 mm, 0.2 mm thickness, lot. 4755071) was supplied by Kojundo Chemical Lab. Co., Ltd. CH₄ gas (>99.0% purity, PURE grade) was purchased from Sumitomo Seika Chemicals Co., Ltd. and used for chemical vapor deposition. Ar gas (>99.9999% purity, G1 grade) was purchased from Taiyo Nippon Sanso Corporation and used in an Ar-filled glovebox. Highly oriented pyrolytic graphite (HOPG, ZYB quality, GRBS/0.6 \times 7 \times 7) was purchased from ScanSens GmbH and used for the wettability test of molten sulfur. The morphology of the composite electrodes was analyzed by field emission-scanning electron microscopy (Hitachi S-4800). Elemental mapping of the samples was conducted using an energy-dispersive X-ray spectrometer (EDAX Inc., Genesis XM2M) attached to an SEM instrument. The accelerating voltages were fixed at 2.0 kV for surface observation and 15 kV for elemental analysis. High-magnification surface analysis was also conducted using a transmission electron microscope (Topcon EM-002B) at an accelerating voltage of 200 kV. The lattice resolution for the TEM measurements was 0.14 nm. The exposure time for the highmagnification TEM measurements was 1-10 s. HAADF-STEM and EDS-mapping of the cathode materials before and after the iterative discharge/discharge cycles were measured on a transmission electron microscope (Thermo Scientific Titan³ 60-300 Double Corrector, FEI-Company) equipped with an energy-dispersive X-ray spectrometer (Super-X). The accelerating voltage was set to 60 kV to prevent the damage to the samples during EDS-mapping in which the scans required long accumulation times. Nitrogen physisorption measurements were conducted at 77 K using a volumetric sorption analyzer (BEL Japan, Belsorp max). The specific surface area $(S_{\text{BET}} \text{ in } m^2 \text{ g}^{-1})$ was calculated according to the Brunauer-Emmett-Teller (BET) method in the pressure range of $P/P_0 = 0.05 - 0.35$ for the mesoporous materials and $P/P_0 = 0.01-0.05$ for the microporous materials as previously described.⁵⁸ The mesopore size distribution was calculated via the Barrett-Joyner-Halenda (BJH) method applied to the N₂ adsorption isotherms.⁵⁸ Wide-angle powder XRD patterns of the samples were recorded using an X-ray diffractometer (Rigaku, MiniFlex 300/600) with Cu K α radiation (λ = 1.5406 Å) generated at 40 kV and 15 mA. The Raman spectra were obtained at room temperature by excitation at 532.2 nm with an Ar laser (100 mW) using a spectrometer (Jasco NRS-3300FL). The exposure time for the measurements was 120 s, and 10 scans were accumulated. The Raman shift was calibrated to the G-band of the external standard, HOPG (1582 cm⁻¹),⁶⁹ and the intensity of the Raman scattering was also normalized to the G-band. The S content in the carbon scaffold was determined using a thermogravimeter (Shimadzu, DTG-60H) operating from 300 to 873 K at a rate of 10 K min⁻¹ under a steady flow of N₂. The amounts of carbon edge sites (N_{edge}) were quantified by TPD methods as previously reported.^{61,67,70°} The TOF-SIMS spectra were collected using a spectrometer (TOF.SIMS5, ION-TOF GmbH) in the bunching (high mass resolution mode) positive mode. The primary ion for TOF-SIMS was Bi⁺ (25 kV and 1.0 pA).

2.2. Synthesis of Carbon Materials. Previously, NPG with an average pore size of 5.8 nm was synthesized using γ -alumina nanoparticles (TM-300, average particle size of 7 nm).⁵⁸ In this study, NPGs with large pore sizes and large pore volumes were synthesized as follows: Commercially available θ -alumina nanoparticles (TM-100, Taimei Chemicals Co., Ltd., average particle size of 15 nm) with a BET surface area of 120 m² g⁻¹ were used as the nanosized template for the synthesis of single-walled 3D graphene. TM-100 (2.05 g) was mixed with quartz sand (6.73 g, Wako Pure Chemical Industries) in a weight ratio of 3:10. The mixture was placed in a quartz chamber fixed in a gold furnace and heated to 1173

K (900 °C) at a rate of 10 K min⁻¹ under a steady flow of Ar (800 mL min⁻¹). The temperature was maintained for 30 min, and a mixture of CH_4 (20 vol %) and Ar (80 vol %) was then introduced into the chamber for 110 min at 1173 K for θ -alumina nanoparticle-catalyzed chemical vapor deposition of methane. The temperature was maintained for 30 min under Ar. The chamber was then cooled down to room temperature, and the quartz sand was separated by sieving. The weight ratio of carbon deposition in the carbon/alumina composite was determined via thermogravimetry to calculate the average number of graphene layers as described later. The obtained carbon/alumina composite was immersed in an aqueous solution of HF (47 wt % and 100 g) at room temperature for 5 h with agitation using a shaker (Recipro Shaker NA-201 N, Nissin) to remove the template. Then, the aqueous solution was filtered using a hydrophilic PTFE membrane filter (Advantec H100A047A, Toyo Roshi Kaisha, Ltd., $\phi = 1.00 \ \mu m$), and the residue was washed with an aqueous solution of HF (47 wt % and 200 g) and water several times. When more than 2 g of alumina was used, the template was not fully removed. In this case, the chemical etching process with HF was repeated. After filtration, the wet sample was immersed in an organic solvent (acetone or isopropyl alcohol), and the mixture was stirred at 323 K (50 °C) for 8 h. Water was substituted with organic solvents to prevent the graphene architecture from shrinking under the intense capillary force of water. The solvents were then filtered off on a hydrophilic PTFE membrane, and the obtained carbon was dried under vacuum at 373 K (100 °C) overnight to give the nanoporous graphene (NPG⁹⁰⁰, 185 mg). The average number of graphene walls was calculated to be 1.0 by the TG analysis (Figure S1) using an equation mentioned in the Supporting Information. NPG⁹⁰⁰ was then annealed at 2073 K (1800 °C) for 1 h under vacuum to coalesce the carbon edge sites, yielding NPG¹⁸⁰⁰ (Figure 1b).



Figure 1. (a) TEM image of NPG⁹⁰⁰. (b) Schematic of the edge fusion in NPG⁹⁰⁰ by thermal treatment to give NPG¹⁸⁰⁰. (c) Raman spectra of NPG⁹⁰⁰ and NPG¹⁸⁰⁰. λ_{ex} = 532 nm. The strong D-band of NPG¹⁸⁰⁰ is due to the fused region⁵⁸ rather than the edges.⁷⁴

2.3. Cathode Preparation and Characterization. The cathode composites were prepared by impregnating sulfur (200 mg and 50 wt %) into a carbon material (40 mg and 10 wt %) at 443 K (170 °C) using an autoclave for 6 h followed by ball milling of the mixture and LPS (160 mg and 40 wt %) at 370 rpm for 15 h using a ZrO_2 pot and Zr_2O ball (40 g). Ball milling was performed in a grinder (Fritsch, Premium-Line P-7) with 5.34 G. All the preparation processes were conducted in an Ar-filled glovebox or under an Ar atmosphere. Because the Li⁺ conductivity of LPS decreases when it is heated beyond 493 K (220 °C),⁷¹ the cathode composites were carefully handled throughout the preparation. The cathode composites obtained using NPG⁹⁰⁰, NPG¹⁸⁰⁰, and MSC30 were denoted as S@ NPG⁹⁰⁰ + LPS, S@NPG¹⁸⁰⁰ + LPS, and S@MSC30 + LPS,

respectively, and they were analyzed via FE-SEM, XRD, Raman spectroscopy, and HAADF-STEM/EDS.

2.4. Cell Assembly. KP-SolidCell was purchased from Hohsen Corp. and used for all the electrochemical investigations. Li₁₀GeP₂S₁₂ (LGPS) enjoys an extremely high lithium ionic conductivity¹⁰ and electrochemical stability,⁶⁶ and therefore, we used LGPS as a solidstate electrolyte for the binder separating the cathode and anode parts. The cells for the all-solid-state Li-S batteries were assembled as follows: 80 mg of LGPS as the solid electrolyte was weighed, placed in a mold with $\phi = 10$ mm, and pressed at 400 MPa for 3 min. The use of a smaller amount of LPGS may lead to short-circuit between the anode and cathode. Then, 5.0 mg of the cathode composite (S@ carbon + LPS) was loaded onto the surface of the LGPS pellet and pressed again at 400 MPa for 3 min. While pressing achieves a densely packed pellet for better electrochemical performance,66 the high pressure (~600 MPa) causes the formation of cracks, as confirmed by SEM. An In foil ($\phi = 9 \text{ mm}$ and 0.2 mm thickness) and a Li foil ($\phi = 8$ mm and 0.2 mm thickness) were placed on the anode side of the cell and pressed at 100 MPa for 1 min to give a Li-In composite as the reference/counter electrode. The use of Li-In alloy at an interface between the Li and solid electrolyte layer is indispensable for good cyclability and high rate capability for all-solid-state cells.⁷² The Li-In/LGPS/(S@carbon + LPS) pellet was sandwiched between a pair of stainless discs as the current collector, held on a T-type cell, and fastened at 28 N·m (112 MPa) using a torque wrench. Fastening is crucial for high cell performance because an intimate contact between the solid electrolyte and the cathode counterparts lowers the resistance at the grain boundaries.^{42,43,73} The assembly process was performed under an Ar atmosphere in a glovebox.

2.5. Electrochemistry. The electrochemical properties of the assembled cells were investigated by galvanostatic charge/discharge measurements using a multi-channel galvanostat (Hokuto Denko Corp.) under a constant current (CC) or constant current-constant voltage (CCCV) with a rate of 0.2-2C in the CC region. Herein, 1C is defined as the rate at which a given cell requires 1 h for full conversion between a charged and a discharged state under a constant current. As such, "0.2C" indicates the rate that requires 5 h for the full conversion between the fully charged and discharged state of the cell, while "2C" indicates that the full redox process is expected to finish within 30 min. The cells were placed in a heater with a temperature controller (hot air rapid drying oven SOYOKAZE, Isuzu) for all the electrochemical investigations, and the charge/discharge measurements were performed at 353 K (80 °C). The electrolyte decomposes, and carbon reacts with Li at potentials lower than 0.4 V versus Li-In;⁴³ therefore, the electrochemical analysis was conducted between 0.5 and 2.5 V versus Li-In. The potential was reported as those versus the Li-In anode, and the potential versus the Li⁺/Li redox couple was calculated as follows: $E_{\text{versus Li}+/\text{Li}} = E_{\text{versus Li}-\text{In}} + 0.62 \text{ V.}^3$ For the durability test of the assembled cells, the first cycle was conducted at a rate of 0.2C under the CCCV conditions, and the durability properties were investigated from the second cycle at a rate of 2C under the CC conditions. Post-analysis by HAADF-STEM/ EDS and TOF-SIMS was conducted after the iterative four or five sets of discharge/charge experiments at rates of 0.2, 0.5, 1, and 2C. The direct current resistance (DCR) was determined using the voltage drop of an assembled cell upon discharge at rates of 0.2, 0.5, 1, and 2C from 50% of the state of charge (SOC) at temperatures ranging from 333 K (60 °C) to 363 K (90 °C).

3. RESULTS AND DISCUSSION

3.1. Characterization of Materials. First, NPGs were synthesized using θ -alumina nanoparticles with an average particle size of 15 nm as the template and analyzed *via* XRD, TGA, N₂ physisorption, TEM, Raman spectroscopy, and FE-SEM. CH₄ is typically inert,⁷⁵ but the surfaces of alumina nanoparticles expedited the carbonization of gaseous hydrocarbon at 1173 K (900 °C), and the subsequent chemical etching using HF gave NPG⁹⁰⁰. The number of graphene layers

Table 1.	Summary	of the	Physicochemical	Properties	of Materials
				1	

	$V_{\rm p}/{ m mL}~{ m g}^{-1}$				-1					
materials	$S_{\rm BET}/{\rm m}^2~{\rm g}^{-1}$	d _{p,BJH} ∕nm	total	micro ^a	meso ^b	packing ratio of S ^c	packing ratio of Li ₂ S when fully discharged ^d	$\sigma^e/{ m S~cm^{-1}}$	$N_{\rm edge}^{f}/{\rm mmol}~{\rm g}^{-1}$	<i>K^g/</i> GPa
NPG ⁹⁰⁰	2300	9.2	5.30	0.85	4.5	47%	81%	0.52	3.1	0.90
NPG ¹⁸⁰⁰	1910	9.0	4.10	0.70	3.4	61%	105%	0.97	0.16	0.30
MSC30	2841	2.3	1.6	0.92	0.7	156%	268%	1.29	2.3 ⁷⁰	1.57
S								5×10^{-30h}		$6-7^{76}$

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^{*a*}Obtained from the DA plot. ${}^{b}V_{\text{meso}} = V_{\text{total}} - V_{\text{micro}}$. ^{*c*}The value was calculated based on the 5:1 weight ratio of S:C using the pore volume $(V_{\text{p,total}})$ and the density of sulfur $(\sigma_{\text{S}} = 2 \text{ g cm}^{-3})$: $5 \div \sigma_{\text{S}} \div V_{\text{p}} \times 100$. ^{*d*}The value was calculated based on the 5:1 ratio of S:C using $V_{\text{p,total}}$ the density of Li₂S $(\sigma_{\text{Li2S}} = 1.67 \text{ g cm}^{-3})$, and the molecular weights (M_{w}) of Li₂S (45.95) and S (32.065): $M_{\text{w,Li2S}} \div M_{\text{w,S}} \times 5 \div \sigma_{\text{Li2S}} \div V_{\text{p}} \times 100$. ^{*e*}Determined at an applied pressure of 90 MPa. ^{*f*}Amount of edge sites (N_{edge}) calculated by using the TPD results (Figure S3). ^{*g*}The bulk moduli (*K*) of the samples were determined from the linear part of the stress-strain curve at a pressure of approximately 50 MPa, as shown in Figure S4 and with eq S3. ^{*h*}The value was derived from a literature. ⁴³

 (n_{ora}) was nominally calculated to be 1.0 based on the TGA result (Figure S1) coupled with eqs S1 and S2. The XRD pattern of NPG⁹⁰⁰ showed no peak originating from θ -alumina, indicating that the template was successfully removed (Figure S2). A very weak diffraction of 002 planes indicates suppressed graphene stacking, while a peak at $2\theta = 43^{\circ}$ corresponding to the diffractions of 10 planes for graphene in NPGs⁵⁸ demonstrates the development of a graphene structure in NPGs. Annealing of NPG⁹⁰⁰ under an inert atmosphere at 2073 K (1800 °C) for 1 h fused the H-terminated edges to give a more continuous and conductive NPG¹⁸⁰⁰ (Figure 1b), as confirmed by the evolution of H_2 (Figure S3).⁵⁸ Measurements of N2 physisorption on cubic NPGs revealed that the gravimetric surface area ($S_{BET} = 1910-2300 \text{ m}^2 \text{ g}^{-1}$) approached that of ideal 2D graphene (2627 m² g^{-1}), supporting the formation of single-layered carbon. The mean spherical diameter was 9 nm, and the pore volumes reached up to 5.3 mL g⁻¹. The obtained pore distribution in NPGs was corroborated by the TEM image (Figure 1a). The peak at 2θ = 22° for 002 diffractions of the stacked graphene structure (= graphite) was weak for NPGs (Figure S2), supporting that graphene stacking was less dominant. To confirm the formation of a continuous graphene layer, we examined the Raman spectra of the obtained carbons. The stacked graphene layers in HOPG showed a Raman active E_{2g} band (so-called Gband) at 1582 cm⁻¹ and a G'-band at 2727 cm⁻¹, while singlelayered graphene is expected to give an upshifted G-band at 1587 cm⁻¹ and a downshifted G'-band at around 2690 cm^{-1.68,69} The Raman shifts of the **NPGs** corresponding to the G- and G'-bands were close to the latter values (Figure 1c). Especially, the G'-band was significantly intensified upon annealing at 2073 K, corroborating the growth of singlelayered graphene in the 3D carbon framework.⁵⁸ Hgporosimetry of the obtained NPGs showed that the bulk moduli were small (Figure S4), indicating the flexibility of single-walled graphene with a smaller curvature. These indicate the development of a graphene structure in the 3D nanoarchitecture with the layer stacking being less dominant. By the way, the contact angle of molten sulfur on HOPG that is a stacked but flat equivalent of NPGs was ~38° at 413 K (140 °C), and such a good wettability of molten sulfur on the surface of hexagonally arranged carbons is conducive to the incorporation of sulfur into the mesopores of curved 3D graphene. Indeed, the pore volume of NPG^{900} (5.30 cm³ g⁻¹) and the typical density of sulfur (2 g cm^{-3}) indicate that 1 g of NPG⁹⁰⁰ can accommodate 11 g of sulfur in its mesopores (Table 1). Therefore, the obtained 3D graphene materials were

combined with sulfur for use as a conductive additive in all-solid-state Li–S batteries (Figure 2a). As a reference, an activated carbon (MSC30)-based composite was also prepared because MSC30 is reported to be an excellent conductive additive.³⁵



Figure 2. (a) Schematic of the preparation of cathode composites showing the introduction of S into curved 3D mesoporous graphenes and the addition of a solid electrolyte by mixing. The photograph shows a droplet of molten sulfur on HOPG at 413 K for the wettability test. The picture of **NPG** is reprinted from. (b) N₂ physisorption isotherms of **NPG**⁹⁰⁰ (dashed line) and S@**NPG**⁹⁰⁰ (solid trace) at 77 K. (c) Raman spectra of **NPG**¹⁸⁰⁰ and S@**NPG**¹⁸⁰⁰ prepared by impregnation at 433 K. Journal of Power Sources from ref 61 copyright (2020) with permission (no. 5117540323056) from Elsevier

The incorporation of sulfur into the mesopores of the carbon materials was achieved in a closed reactor at 443 K (170 °C) for 6 h, and this was confirmed by the reduced N₂ uptake at 77 K (Figure 2b), Raman spectra (Figure 2c), TGA (Figure S5), XRD patterns (Figure S6), and SEM images (Figure S7) of the composites before and after the impregnation. Hereafter, the hierarchical composites were denoted as S@NPG⁹⁰⁰, S@NPG¹⁸⁰⁰, and S@MSC30. Figure 2b shows that S@NPG⁹⁰⁰ showed the presence of a macropore, while there was almost no microporosity and mesoporosity as compared with NPG⁹⁰⁰. As a consequence, the gravimetric surface area of S@NPG⁹⁰⁰ after impregnation (S_{BET} ~40 m² g⁻¹) was significantly lower than that of NPG⁹⁰⁰

 $(S_{\text{BET}} = 2.3 \times 10^3 \text{ m}^2 \text{ g}^{-1})$. TGA showed that pristine sulfur completely sublimated at temperatures lower than 560 K, while the weight of the sulfur/carbon composites gradually decreased (Figure S5). The weight ratio of sulfur and carbon in the composites was calculated to be 5:1 from Figure S5. The XRD patterns of S@NPG⁹⁰⁰ showed that the peaks corresponding to α -sulfur were weak (Figure S6). Therefore, the sulfur crystallites were significantly small within the nanopores, which is crucial for a higher specific charge/discharge capacity.^{30–37,44} Moreover, small-angle scattering of the porous materials was suppressed after impregnation (Figure S6 inset), further supporting that sulfur was successfully incorporated into the nanopores. In addition, the SEM images of NPG⁹⁰⁰ before and after the impregnation were almost identical, although their weights differed by a factor of 6 (Figure S7). In the Raman spectra, the G'-band of $S@NPG^{1800}$ upshifted by 16 cm⁻¹ from that of pristine NPG¹⁸⁰⁰ at 2670 cm⁻¹ with the intensities and positions of the G-band at 1588 $\rm cm^{-1}$ and the 2G'-band⁶⁹ at 3250 cm⁻¹ being almost identical for the two materials (Figure 2c), suggesting the intimate contact between sulfur and graphene structures. These results suggested that sulfur was efficiently incorporated into the mesopores of NPGs. On the contrary, MSC30 has a smaller pore volume (Table 1), and therefore, it is impossible for all sulfur to be incorporated in the nanopores under the condition investigated (vide infra).

3.2. Electrochemical Performance. With this in mind, we then prepared cathode composites of S@NPGs and LPS,³⁰ with a weight ratio of 60:40, by conventional ball-milling.^{30-37,44} Finely ground powder was obtained (Figure 3) as



Figure 3. SEM images of (a-c) S@NPG⁹⁰⁰ + LPS, (d-f) S@NPG¹⁸⁰⁰ + LPS, and (g-i) S@MCS30 + LPS.

compared with the original materials before milling (Figure S8), and HAADF-STEM coupled with EDS of the prepared composites revealed that carbon, sulfur, and phosphorus atoms were efficiently mixed on the nanoscale (Figure S9), supporting the XRD results. The electrochemical performance of the cathode composites was then investigated in an all-solid-state configuration with Li–In alloy as the anode, $Li_{10}GeP_2S_{12}$ crystal with a high Li⁺-conductivity of 12 mS cm⁻¹ at room temperature¹⁰ as the solid-state electrolyte, and S@NPGs + LPS as the cathode. When assembled, the all-solid-state cell was in the fully charged state, and the initial cell voltage of the assembled cell with S@NPG⁹⁰⁰ was 1.87 V versus Li–In. This value was 0.14 V lower than that of the assembled cell with S@

MSC30 (E_{ini} = 2.11 V vs Li–In). Nevertheless, the discharge plateau of the cell using S@NPG⁹⁰⁰ (1.4 V vs Li-In) was identical to that using S@MSC30 (Figure 4a). A value of approximately 2.1 V versus Li⁺/Li is close to the equilibrium potential of the liquid-based Li–S battery at full lithiation (S_8 + 16Li \leftrightarrow 8Li₂S; E = 2.2 V vs Li⁺/Li).⁵⁷ Therefore, these results indicated that the S@NPG900-based cathode gave an ideal redox reaction between S₈/Li and Li₂S during battery operation. Indeed, the capacity of cells with $S @ NPG^{900} +$ LPS (716 mA h per gram of the cathode, corresponding to 4.56 mA h cm⁻² or 1430 mA h gS⁻¹) was better at 0.2C, and this corresponds to 86% of the nominal sulfur utilization. The specific capacity in terms of the cathode weight is the highest value so far reported in all-solid-state Li-S batteries (Table S1). The decrease in the potential of the as-prepared cell suggests that sulfur incorporated into the mesopore of 3D graphene could be stabilized, and this is in good agreement with the Raman spectra, TGA, and HAADF-STEM/EDS analysis showing a better interplay and mixing between the surfaces of NPGs and sulfur.

The specific capacities of the all-solid-state cells for the CC region were further investigated at various rates (Figure 4b). When charged at 2C, the cell with S@MSC30 as the cathode component retained 17% of the capacity at 0.2C. In contrast, the specific capacity of the cell comprising S@NPG⁹⁰⁰ was 211 mA h g⁻¹ at 2C, which is 33% of the capacity at 0.2C. To understand the rate characteristics, the temperature dependence of the DCR in the assembled cells (Figure 4c) was analyzed using the following equation:

$$\sigma T = \sigma_0 e^{-E^*/k_{\rm B}T} \tag{1}$$

where σ is the conductivity in S cm, T is the temperature, σ_0 is the pre-exponential constant, $k_{\rm B}$ is the Boltzmann constant, and E^{\ddagger} is the activation barrier of ionic hopping. The semiconducting feature shown in Figure 4c follows the Nernst-Einstein relationship, which indicates that ionic conductivity is the bottleneck during battery operation, and Li⁺-conductivity across the lithium thiophosphate glass^{30,77} will be crucial for the full utilization of sulfur atoms. The activation barrier for carrier hopping was 0.15 eV for the NPG⁹⁰⁰-based cell and 0.12 eV for the MSC30-based cell. Thus, the mixing morphology of NPGs with a continuous graphene structure may be less advantageous than that of MSC30 for ionic conduction, and this led to poor performance at lower temperatures. Nevertheless, the ionic conductivity of the NPG⁹⁰⁰-based cell at 353 K was better than that for the MSC30-based cell, and this could rationalize the cell performance at high temperatures, as shown in Figure 4b.

The Coulomb efficiency was near unity after a few discharge/charge cycles. Therefore, cycle stability was tested at a specific temperature and rate. As shown in Figure 4d, good capacity retention even after 500 cycles was observed for the **NPGs**-based cells, whereas relatively fast degradation in cell performance was observed for the S@MSC30-based cell. The half-life for the MSC30-based cell was 186 cycles, while that for the **NPG**⁹⁰⁰-based cell was approximately 4 times longer (732 cycles). The **NPG**¹⁸⁰⁰-based cell showed much better durability with a half-life of 912 cycles.

 NPG^{1800} s were chemically and electrochemically stable because of the fewer reactive edge sites in the seamless graphene structure.^{58,59} Indeed, NPG^{1800} contained a one order of magnitude smaller amount of edge sites ($N_{edge} = 0.16$

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Figure 4. (a) Charge/discharge profile of Li–In/LGPS/S@C + LPS cells at a rate of 0.2C. (b) Specific capacities of the all-solid-state cells for the charge process (Li₂S \rightarrow 2Li + S) with S@NPG⁹⁰⁰ (red), S@NPG¹⁸⁰⁰ (blue), and S@MSC30 (black trace) at various rates from 0.2C to 2C under the CCCV condition. (c) Nernst–Einstein plot for the direct current resistance of Li–In/LGPS/S@C + LPS cells at various temperatures at a state of charge of 50%. (d) Durability test of the all-solid-state cells with S@NPG⁹⁰⁰ ($E_{ini} = 1.91$ V, red), S@NPG¹⁸⁰⁰ ($E_{ini} = 1.92$ V vs Li–In, blue), and S@MSC30 ($E_{ini} = 2.07$ V, black trace) at a rate of 2C (10.6 mA cm⁻² and 1.67 A g⁻¹) from the 10th cycle. The specific capacity denotes the capacity *per* gram of cathode composite. Figure S10 shows the representative time course of the discharge/charge results.

mmol g^{-1}) than the other carbons (Table 1 and Figure S3). Consequently, the cubic structure of 3D graphene was retained even after the electrochemical investigation, as confirmed by the TEM analysis following the removal of sulfur and the solid electrolyte using organic solvents (Figure S11). This maintenance of the carbon structure in NPG¹⁸⁰⁰ was also supported by the corresponding SAED showing 10 and 11 peaks of graphene. This will rationalize the better electrochemical stability of the NPG^{1800} -based cathode, as shown in Figure 4d. On the contrary, MSC30 is an activated carbon containing numerous chemically active edge sites ($N_{edge} = 2.3$ mmol g⁻¹, Table 1),^{58,70} and its electrochemical instability during all-solid-state cell operation may be the reason for performance degradation. However, this cannot explain the reason why the NPG900-based cathode showed better longterm stability than the MSC30-based cathode. To understand this observation, HAADF-STEM/EDS of the assembled cells was conducted before and after the electrochemical cycles. As shown in Figure 5a-j, the elemental distribution was uniform even after the iterative chemical conversions for the NPGbased cathode composites. A homogeneous distribution of sulfur and phosphorus was also observed for the original composite of the MSC30-based cathode (Figure 5k-o). However, a post analysis of the cathode after discharge/charge cycles of the assembled cell revealed that sulfur was isolated as a bulk of a few hundreds of nanometers (Figure 5s). This phase segregation was complemented by a TOF-SIMS analysis of the Li⁺ distribution (m/z = 6 and 7) in the cathode components (Figure 6a). Before palletization, the surfaces of both the NPG-based and MSC30-based cathodes were rough, as shown in Figure 3. After palletization and subsequent cycle tests, Li⁺ distribution was uniform in the NPG-based cathode, indicating the presence of a homogeneous network for Li⁺conduction. In contrast, TOF-SIMS of the MSC30-based cathode after the same investigation showed the non-uniform



Figure 5. (a,f,k,p) HAADF-STEM and (b-e, g-j, l-o, and q-t) EDS-mapping of the cathode composites for $S@NPG^{900}$ + LPS before (a-e) and after (f-j) 20 cycles of the iterative discharge/charge investigation. S@MSC30 + LPS (k-o) before and (p-t) after 16 cycles of the iterative discharge/charge investigation.

distribution of Li^+ ; the area for poor lithium distribution would be complemented to an abundance of sulfur, which corroborated the phase segregation shown in Figure 5.

Although a continuous structure improves the flexibility and chemical/electrochemical stability of **NPGs**, the morphology of the mixed compound is somewhat unfavorable, as shown in Figure 3. Nevertheless, a large pore volume (up to 5.3 mL g⁻¹) that can accommodate more than 5 g of sulfur *per* gram of **NPGs** demonstrates that the bulk-heterojunction comprising nano-confined insulating and inflatable sulfur is durable even after electrochemical discharge/charge cycles. The elastically



Figure 6. (a) Li⁺-mapping of the cathode surfaces by TOF-SIMS in the positive mode (left) before the palletization and (right) after discharge/charge cycle tests. Relatively homogeneous distribution of Li⁺ was observed for S@NPG⁹⁰⁰ + LPS, while phase segregation was observed for S@MSC30 + LPS. (b) Schematic of phase segregation of insulating sulfur at high rates with high sulfur loadings of 50–60 wt % after electrochemical investigations at 353 K.

deformable architecture of continuous mesoporous graphenes,⁶⁰ demonstrated by the Hg-porosimetry (Figure S4), would also facilitate the solid-state reactions by buffering and conforming to the volume changes that occur during the electrochemical processes.

High-loading of insulating active materials is usually impracticable, but the initial capacity of the NPG⁹⁰⁰-based cathode system was 716 mA h *per* gram of cathode (4.56 mA h cm⁻²) at 353 K, even with one of the highest loadings of the active material (50 wt %, Table S1) in the cathode composite. A higher loading (60 wt %) was also tolerated at 353 K (Figure S12), demonstrating the substantial efficacy of the high pore volume flexible carbon in the cathode composites for commercialization in the future. The development and application of conductive porous materials with high pore volume can further improve the electrochemical reactions in the all-solid-state Li–S batteries by achieving durable interfaces.

4. CONCLUSIONS

The nanostructure of cathode composites for all-solid-state Li–S batteries was controlled by using a mesoporous 3D graphene material as the conductive cathode support to achieve an efficient interface between insulating sulfur and the conductive support. Post-analysis of the cathode components by HAADF-STEM/EDS for elemental distributions and by TOF-SIMS for Li⁺ distribution (m/z = 6 and 7) revealed that

phase segregation in the cathode composites occurred on the microscale because cathode composites degraded at high loadings of the active material and at high rates, which are prerequisites for practical application. Nanostructured 3D graphene with high pore volume can accommodate insulating sulfur to achieve efficient retention of the atoms in the composite during lithiation even after the harsh discharge/ charge processes. Therefore, the resulting cells exhibited better performance durability than the cell using an activated carbon with a smaller pore volume. The chemical and electrochemical stability of the continuous and flexible 3D graphene cage was also confirmed by post analysis. As a result, operating the allsolid-state battery under a harsh condition at 353 K was feasible, and good capacity retention was achieved even after 500 cycles for the NPG-based cells. In addition, the highest specific discharge capacity of 716 mA h per gram of cathode $(4.6 \text{ mA h cm}^{-2})$ was realized with 50 wt % S at 0.2C. Moreover, an initial discharge capacity of 535 mA h per gram of cathode $(3.4 \text{ mA h cm}^{-2})$ was obtained even with an unprecedentedly high loading (60 wt %) of insulating sulfur in the cathode composite. Thus, the high pore volume and high electrochemical stability of elastically flexible single-walled 3D graphene are favorable for the reversible redox process accompanied with a significant volume change by the nanoconfinement of sulfur in the nanopores of NPGs, which achieved a durable three-phase contact between the solid electrolyte, insulating sulfur, and electrically conductive carbon. Further development of the interfaces by a wetprocess⁴⁹ and tuning of the material properties, including pore volume, will further improve the efficiency of the electrochemical processes, and these investigations are underway.

ASSOCIATED CONTENT

I Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c10275.

Results for thermogravimetry, X-ray diffraction, temperature-programmed desorption, Hg porosimetry, scanning electron microscopy, high-angle annular dark fieldscanning transmission electron microscopy coupled with energy-dispersive X-ray spectroscopy, and electrochemistry (PDF)

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Notes

The authors declare no competing financial interest.

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