

## Electrochemistry

# Three-Dimensional Graphene/Ag Aerogel for Durable and Stable Li Metal Anodes in Carbonate-Based Electrolytes

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**Abstract:** The use of Li metal as the anode for Li-based batteries has attracted considerable attention due to its ultrahigh energy density. However, the formation of Li dendrites, uneven deposition, and huge volume changes hinder its reliable implementation. These issues become much more severe in commercial carbonate-based electrolytes than in ether-based electrolytes. Herein, a rationally designed threedimensional graphene/Ag aerogel (3D G-Ag aerogel) is proposed for Li metal anodes with long cycle life in carbonatebased electrolytes. The modified lithiophilic nature of G-Ag aerogel, realized through decoration with Ag NPs, effectively decreases the energy barrier for Li nucleation, regulating uniform Li deposition behavior. Moreover, the highly flexible, conductive 3D porous architecture with hierarchical mesopores and macropores can readily accommodate deposited Li and ensures the integrity of the conductive network during cycling. Consequently, high coulombic efficiency (over 93.5%) and a significantly long cycle life (1589 h) over 200 cycles, with a relatively high cycling capacity of 2.0 mAh cm<sup>-2</sup>, can easily be achieved, even in a carbonatebased electrolyte. Considering the intrinsic high voltage windows of carbonate-based electrolytes, matching the G-Ag aerogel Li metal anode with a high-voltage cathode can be envisaged for the fabrication of high-energy-density Li secondary batteries.

### Introduction

Lithium-ion batteries (LIBs) have dominated the consumer electronics market since their first release by the Sony Corporation in the early 1990s.<sup>[1]</sup> However, even the state-of-the-art LIB technology can no longer meet the ever-increasing demand for high-energy-density batteries in emerging applications such as electric vehicles and large-scale energy storage. This is because the specific capacity of commercial graphite-based anode materials has reached its theoretical lithium storage limit (corresponding to only 372 mAh g<sup>-1</sup>).<sup>[2]</sup> Li metal is considered to be one of the most promising anode candidates owing to its ultrahigh theoretical specific capacity (3860 mAh g<sup>-1</sup>) and its lowest negative electrochemical potential (-3.04 V vs. standard hydrogen electrode) compared to all other anodes.<sup>[3]</sup>

Li metal anodes have continuously attracted widespread attention since the 1970s. However, early attempts to commerci-

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alize Li secondary batteries with metallic Li as an anode by the Exxon Company were ultimately unsuccessful due to the continuous growth of dendritic Li during cycling.<sup>[4]</sup> Uncontrollable dendrite formation during repeated Li plating/stripping as a result of non-uniform mass and charge transfer not only causes "dead Li", giving rise to low coulombic efficiency (CE) and rapid capacity loss, but may also penetrate the separator to contact the cathode, leading to internal short-circuiting.<sup>[5]</sup> Moreover, the related infinite volume expansion during the Li deposition process, owing to its "hostless" nature, may exacerbate breakage of the solid electrolyte interface (SEI) and the electrode structure.<sup>[6]</sup> Consequently, Li dendrites and their related issues severely hinder the practical application of Li metal anodes.

In recent years, remarkable developments in materials science and electrochemistry have made it possible to reconsider the practical use of Li metal anodes. Indeed, numerous strategies have been demonstrated to overcome the aforementioned obstacles. One effective method is to introduce additives into electrolytes. Electrolyte additives, such as  $KNO_3$ ,<sup>[7]</sup> LiNO<sub>3</sub>,<sup>[8]</sup> ethyl  $\alpha$ -cyanoacrylate and LiNO<sub>3</sub> hybrid additive,<sup>[9]</sup> fluoroethylene carbonate (FEC),<sup>[10]</sup> succinic anhydride,<sup>[11]</sup> vinylene carbonate (VC),<sup>[12]</sup> methyl viologen,<sup>[13]</sup> and polysulfide,<sup>[14]</sup> have proved to be beneficial for forming a uniform SEI to inhibit the growth of Li dendrites. Besides in situ formation of an improved SEI through the use of additives, constructing artificial SEI films, such as layers of Li<sub>3</sub>PO<sub>4</sub>,<sup>[15]</sup> dynamically cross-linked polymers,<sup>[16]</sup> lithium phosphorus oxynitride (LiPON),<sup>[17]</sup> Al<sub>2</sub>O<sub>3</sub>,<sup>[18]</sup>

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nanospheres coating,<sup>[19]</sup> poly[(N-2,2-dimethyl-1,3-dioxolane-4methyl)-5-norbornene-exo-2,3-dicarboximide],<sup>[20]</sup> or poly(dimethylsiloxane) thin film,<sup>[21]</sup> by ex situ methods has also been suggested as an advantageous strategy. Although these approaches based on interface modification are promising, the protective effect of SEI films may be severely weakened due to the infinite relative volume change during cycling. Thus, dendrite growth may not be completely eliminated.[22] To address this problem, researchers have demonstrated many rational designs of three-dimensional (3D) current collectors to accommodate Li deposition.<sup>[23]</sup> Among them, 3D conductive matrices based on carbon materials (e.g., layered reduced graphene,<sup>[6]</sup> a carbon nanofiber network,<sup>[24]</sup> a vapor-grown carbon fiber 3D host,<sup>[25]</sup> and a carbon nanotube 3D matrix<sup>[26]</sup>) have exhibited great potential because of their multifunctional roles.<sup>[27]</sup> These 3D porous carbon matrices not only provide enough free volume to accommodate Li plating, but also help to lower the local current density and suppress the formation of Li dendrites.<sup>[28]</sup> However, most carbon materials are not "lithiophilic", binding only weakly with Li, inducing a large overpotential for Li nucleation.[29]

Recently, Cui et al. found that noble metals having a definite Li solubility (for example, Ag, Au, and Pt) are typically lithiophilic, presenting no energy barrier for Li nucleation.<sup>[3,30]</sup> Based on this, Hu et al. introduced Ag nanoseeds on carbon nanofibers as an Li metal anode, which exhibited stable cycling over 500 h at 0.5 mA cm<sup>-2</sup> for 1 mA h cm<sup>-2</sup> in an ether-based electrolyte.<sup>[31]</sup> Although significant progress has been made, there are still many challenges in applying Li metal anodes in commonly used carbonate-based electrolyte systems (the voltage windows of carbonate-based electrolytes are generally wider than those of ether-based electrolytes, and may thus be compatible with high-voltage cathodes). Moreover, a larger cycling capacity ( $\geq 2$  mAh cm<sup>-2</sup>) is also highly desired.

In this study, a well-designed 3D graphene aerogel decorated with Ag nanoparticles (G-Ag aerogel) has been developed as an Li metal anode with long cycle life and high coulombic efficiency in carbonate-based electrolytes. It was fabricated by a one-step hydrothermal reaction followed by freeze-drying and annealing treatment (Figure 1a); more details of the syn-





**Figure 1.** (a) Schematic illustration of the synthetic procedure for obtaining the G-Ag aerogel. (b) Schematic representation of Li deposition on the G-Ag aerogel.

thetic procedure are given in the Experimental Section. In this unique structure, graphene sheets are interconnected to form a robust 3D porous conductive network. Ag NPs homogeneously embedded in graphene create stable Li nucleation sites to induce uniform deposition of Li metal on the graphene sheets (Figure 1 b). Through these advantageous features, as a free-standing Li metal anode, the G-Ag aerogel can effectively inhibit the growth of Li dendrites, leading to improved cycling stability.

### **Results and Discussion**

The XRD pattern of the G-Ag aerogel is shown in Figure 2a. The sharp peaks at 38.1°, 44.3°, 64.4°, 77.4°, and 81.6° correspond to the (111), (200), (220), (311), and (222) diffractions, respectively, of cubic crystalline Ag (JCPDS no. 089–3722). The broad feature centered at 26.5° may be attributed to both crystalline and disordered graphite phases in graphene.<sup>[32]</sup> The G-Ag aerogel has a relatively high specific surface area of 277.6 m<sup>2</sup>g<sup>-1</sup> with hierarchical mesopores and macropores and a pore volume of 0.25 cm<sup>3</sup>g<sup>-1</sup> (Figure 2b). This guarantees reduction of the local current density and a uniform charge distribution during Li deposition.



Figure 2. (a) XRD pattern of G-Ag aerogel. (b) Nitrogen adsorption and desorption isotherms of G-Ag aerogel (the inset shows the corresponding pore size distribution).

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The morphology of the G-Ag aerogel was studied by SEM and TEM. The interconnected 3D porous G-Ag aerogel is composed of randomly wrinkled graphene sheets in tight contact with one another, in which there are many pores and voids (Figure 3 a). Ag NPs are evenly enwrapped or encapsulated by



Figure 3. (a, b, c) SEM images, and (d) elemental mappings of the G-Ag aero-gel.

the crumpled graphene layers (Figure 3 b, c). Elemental mapping of the G-Ag aerogel showed Ag to be homogeneously distributed in the C matrix, suggesting uniform incorporation of Ag NPs in the graphene framework (Figure 3 d). The Ag content in the G-Ag aerogel measured by ICP was 7.46 wt%. The Ag contents in G-Ag aerogel samples could be easily controlled by adjusting the amount of  $AgNO_3$  used in the hydro-thermal reaction (Table S1).

TEM images of the G-Ag aerogel (Figure 4a, b) showed Ag NPs in the size range 20–200 nm to be tightly immobilized on the graphene sheets. A high-magnification TEM image of an individual Ag NP (Figure 4c) clearly revealed wrinkles of graphene around it. In the corresponding SAED pattern, the bright symmetrical dots and faint diffraction ring may be assigned to Ag nanocrystals and graphene, respectively. An HRTEM image (Figure 4d) shows a typical Ag NP anchored on the graphene. The internal fringe spacing of about 0.24 nm can be indexed to the (111) reflection of cubic *Fm*-3*m* Ag. The curved and irregular external lattice fringes can be attributed to graphene. The 3D porous structured G-Ag aerogel with high specific surface area not only delays or even inhibits the formation of Li dendrites by decreasing the effective current density, but also provides reliable buffer space for accommodating Li deposition.

In previous research, it has been shown that GO can be reduced to form rGO aerogel through hydrothermal reaction, which can then be used in electrochemical energy storage without further treatment.<sup>[33]</sup> However, the rGO aerogel is only partly reduced, and still bears a large number of oxygen-containing groups. Therefore, we added an extra heat-treatment procedure aimed at further reducing the G-Ag aerogel. Raman spectra of GO and G-Ag aerogel before and after annealing were obtained to monitor the process (Figure 5 a). The spectra of each of the samples featured two broad peaks at  $\tilde{v} \approx 1602$ and 1347 cm<sup>-1</sup>, corresponding to the characteristic G band



**Figure 4.** (a, b) TEM images of G-Ag aerogel. (c) TEM image and (d) HRTEM image of a single Ag NP enwrapped by graphene; the inset in (c) shows the corresponding SAED pattern.



**Figure 5.** (a) Raman spectra of GO, G-Ag aerogel (before annealing), and G-Ag aerogel. (b) High-resolution Ag 3d XPS spectrum of G-Ag aerogel. (c) Curve fit of high-resolution C1s XPS spectrum of G-Ag aerogel. (d) Curve fit of high-resolution C1s XPS spectrum of G-Ag aerogel (before annealing).

(graphite band) and D band (defect sites and disorders) of carbon materials, respectively.<sup>[34]</sup> The  $I_D/I_G$  ratio of G-Ag (1.01) was higher than those of the other two samples (G-Ag (before annealing): 0.95; GO: 0.81). It is generally accepted that upon reduction of GO, new graphitic domains are created, which are smaller than those present before reduction, leading to an increase in the value of  $I_D/I_G$  compared to that of GO.<sup>[35]</sup> Hence, the crystallinity of the G-Ag aerogel was enhanced through the further annealing process.

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XPS measurements were performed to investigate the chemical composition and valence state of the G-Ag aerogel (Figure 5 b-d). The Ag 3d spectrum could be resolved into two separate peaks at 374.4 and 368.4 eV, corresponding to Ag 3d3/2 and Ag 3d5/2, respectively (Figure 5b). The inter-peak separation of 6.0 eV suggests the presence of metallic Ag.[36] As shown in Figure 5 c, d, the C1s peaks of both samples can be assigned to C-C (284.8 eV), C-O (285.9 eV), and C=O bonds (288.1 eV), respectively.<sup>[37]</sup> After annealing, the relative proportion of oxygen-containing bonds to C-C bonds, 0.77, as calculated from the relative peak areas for G-Ag, was lower than that for G-Ag before annealing (1.15), corroborating the effective reduction through heat treatment in an H<sub>2</sub>/Ar atmosphere. It has been reported that deep deoxygenation of rGO is very important for improving its electronic conduction network.<sup>[38]</sup> Indeed, the electrical conductivity of G-Ag measured by the four-point probe powder method was 4.61 S cm<sup>-1</sup>, three times higher than that of G-Ag before annealing  $(1.34 \text{ S cm}^{-1})$ . The well-established conductive framework within the G-Ag aerogel can connect deposited Li, making it an integral part of the electronic conductive network, thus reducing the amount of "dead Li".

Li nucleation overpotential is an informative parameter for evaluating the lithiophilicity of electrodes, whereby an electrode with higher nucleation overpotential tends to induce uneven Li deposition.<sup>[29, 39]</sup> It is generally accepted that the interaction between Li and Cu is weak,<sup>[30,40]</sup> such that an appreciable nucleation overpotential (ca. 59 mV) is observed in the initial discharge voltage curve of a Cu foil electrode. However, the binding energy between Ag and Li is relatively high due to the significant solubility of Ag in Li,<sup>[30]</sup> and Ag NPs distributed on the surface of a G-Ag aerogel can effectively regulate the nucleation sites (Figure S2). Therefore, the initial discharge voltage curve of the G-Ag aerogel was very smooth, and no obvious nucleation overpotential was observed (Figure 6). Considering the specific 3D porous structure, unobstructed conductive network, and good Li metal affinity, the G-Ag aerogel can be expected to offer more uniform Li deposition behavior.

SEM images of a Cu foil electrode and G-Ag aerogel with Li deposition after certain numbers of cycles were acquired to reveal the morphologies of the deposited Li (Figure S3 and





**Figure 6.** Galvanostatic discharge voltage profiles of the Cu foil electrode and G-Ag aerogel during initial Li deposition at  $0.5 \text{ mA cm}^{-2}$ .

Figure 7). The surface of the Cu foil electrode after ten cycles exhibited a mossy-like morphology (Figure S3a), fully covered with fibrous Li dendrites in a random arrangement, forming a loose structure (Figure S3b). This loose structure will cause further non-uniformity of the concentration gradient and electric field, and thus exacerbate the growth of Li dendrites. For the G-Ag aerogel after ten cycles (Figure 7a), the surface was very smooth, and no dendrites protruding upward could be discerned. The graphene sheets were covered by a thin layer of metallic Li with irregular lumps (Figure 7 b), suggesting uniform Li nucleation as a result of the embedded Ag NPs. Cross-sectional images of G-Ag aerogel after ten cycles (Figure 7 c, d) showed the interconnected 3D porous structure to be well retained, indicating that the integrity of the conductive network within the electrode had not been damaged during cycling. After 50 cycles, Li metal plating on the graphene was thicker (Figure 7 e, f), which could still be accommodated within the graphene aerogel framework. Indeed, many pores and voids remained (Figure 7 g, h), demonstrating ample buffer space in the G-Ag aerogel to accommodate volume changes of Li metal during repeated plating/stripping.



Figure 7. SEM images of the G-Ag aerogel at 0.5 mA cm<sup>-2</sup> for 2.0 mAh cm<sup>-2</sup> at the Li deposition state after 10 cycles (a, b) on the surface, and (c, d) on the cross-section, and after 50 cycles (e, f) on the surface, and (g, h) on the cross-section.

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**Figure 8.** Coulombic efficiencies of the Cu foil electrode and G-Ag aerogel with cycling capacity 2 mAh cm<sup>-2</sup> (a) at 0.5 mA cm<sup>-2</sup>, (b) at 1.0 mA cm<sup>-2</sup>. (c) Time-voltage trace of the G-Ag aerogel at 0.5 mA cm<sup>-2</sup> for 2 mAh cm<sup>-2</sup>. Typical voltage profiles of (d) the Cu foil electrode and (e) the G-Ag aerogel at 0.5 mA cm<sup>-2</sup> for 2 mAh cm<sup>-2</sup>. (f) Voltage hysteresis of the G-Ag aerogel during 200 cycles.

To meet the requirements for practical application of LIBs, the area specific capacity of anodes should be more than 2.0 mAh cm<sup>-2</sup>. Thus, we carried out electrochemical tests on the Cu foil electrode and G-Ag aerogel at a cycling capacity of 2 mAh cm<sup>-2</sup> in a carbonate-based electrolyte of 1.0 M LiPF<sub>6</sub> in EC/DEC (1:1) with 5 wt% VC as an additive (Figure 8). Coulombic efficiency (CE) is a critical index for evaluating the availability of Li during cycling. The CE can be calculated from the ratio of the amount of Li removed from the anode to that deposited during every cycle.

Figure 8a shows the CE of a Cu foil electrode and a G-Ag aerogel cycled at  $0.5 \text{ mA cm}^{-2}$  for 2 mAh cm<sup>-2</sup>. The CE of the Cu foil electrode gradually decreased to around 81% during 40 cycles, and then fluctuated dramatically after 70 cycles, implying internal short-circuiting within the cell. Encouragingly, the G-Ag aerogel exhibited excellent long-term cycling stability, with a high CE of over 93.5% after 200 cycles. As shown in Figure 8b, when the testing current density was increased to 1.0 mA cm<sup>-2</sup>, a CE of 93.3% after 200 cycles was obtained (the CEs of control electrodes of graphene aerogel and Ag foil were also investigated (Figure S4)). When the testing current density

was increased to 2.0 mA cm<sup>-2</sup> and 4.0 mA cm<sup>-2</sup> at a cycling capacity of 2.0 mAh cm<sup>-2</sup>, the CE of the G-Ag aerogel electrode was maintained at 94.0% and 93.3%, respectively, after 50 cycles (Figure S5).

Figure 8d, e show typical voltage profiles of Li plating/stripping on the Cu foil electrode and G-Ag aerogel, respectively. The charge voltage profile of the Cu foil electrode from the 71st cycle shows substantial voltage fluctuation, because highly resistive "dead Li" steadily accumulated, reducing the amount of Li that could be removed during cycling. However, the voltage profiles of the G-Ag aerogel are very smooth, with little fluctuation over 200 cycles (the oblique discharge and charge profiles between 0 and 1.5 V may be attributed to the lithiation/delithiation processes of the graphene aerogel). The voltage hysteresis of the G-Ag aerogel at 0.5 mA cm<sup>-2</sup> at a cycling capacity of 2 mAh cm<sup>-2</sup> was only 93 mV after 100 cycles, and less than 200 mV after 200 cycles (Figure 8 f). Compared with the Cu foil electrode (Figure S6), the time-voltage curves of the G-Ag aerogel (Figure 8c and Figure S7) were much more stable, even after an extremely long cycle time of 1589 h (200 cycles). The cycling performance of the G-Ag aerogel at

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higher cycling capacities was also investigated (Figure S8). The maximum amount of Li deposited in the G-Ag aerogel was reached at 10 mAh cm<sup>-2</sup>, corresponding to a high specific capacity of 2702.7 mAh g<sup>-1</sup> (Figure S9).

We also fabricated full cells with an LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> electrode as the cathode in order to study compatibility between the G-Ag anode and a high-voltage cathode. As shown in Figure S10, the G-Ag aerogel–LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> full cell delivered a reversible discharge capacity of 140.0 mAh g<sup>-1</sup> after 83 cycles at 1 C, with a cut-off voltage range from 3.0 to 4.3 V. To better understand the interfacial characteristics, electrochemical impedance spectra of the Cu foil electrode and G-Ag aerogel after 15 cycles are shown in Figure S11. Both plots are composed of one compressed semicircle (in the high-to-medium-frequency region) and a linear decline (in the low-frequency region). The semicircle for the G-Ag aerogel is distinctly smaller than that for the Cu foil electrode, indicating a much reduced charge-transfer resistance of the former.

The cycling stability of the G-Ag aerogel was compared with those of previously reported modified Li metal anodes deployed in carbonate-based electrolytes (Table S2). In terms of cycling capacity, current density, cycle life, and CE, the cycling stability of the G-Ag aerogel Li metal anode developed in this work shows overall superiority. We conclude that the enhanced electrochemical performance of the G-Ag aerogel can be attributed to three outstanding characteristics: (1) graphene sheets are interconnected to form an intrinsic 3D conductive current collector, on which Li metal can be reversibly deposited and removed without losing electronic contact with the matrix; (2) through a combination of rapid charge transfer, a homogeneous distribution of Li<sup>+</sup> ions, and improved lithiophilicity, Li deposition on the G-Ag aerogel is regulated and uniform; (3) deposited Li metal is easily accommodated within buffer spaces in the well-established 3D porous structure, such that the structural integrity of the G-Ag aerogel can be well maintained.

### Conclusions

In summary, a graphene aerogel decorated with homogeneous Ag NPs (G-Ag aerogel) has been prepared by a facile hydrothermal method. The G-Ag aerogel exhibits an interconnected 3D porous structure, which can be compressed and directly used as a freestanding Li metal anode without a binder or a conductive agent. Owing to the prominent advantages of high specific surface area, high electrical conductivity, good lithiophilicity, and unique hierarchically porous architecture, the G-Ag aerogel displays a high CE (over 93.5%) and a long cycle life (1589 h) over 200 cycles, with a relatively high area specific capacity of 2.0 mAh cm<sup>-2</sup> even in carbonate-based electrolytes.

### **Experimental Section**

#### Preparation of G-Ag aerogel

A certain amount of graphene oxide powder (GO, Shanghai Ashine Technology Development Co., Ltd.) was first dispersed in ultrapure water with the aid of ultrasonication to obtain a homogeneous aqueous dispersion of 2 mg mL<sup>-1</sup>. The G-Ag aerogel was synthesized through further optimizing a hydrothermal method reported previously.<sup>[41]</sup> In a typical experiment, a mixture of as-prepared GO aqueous dispersion (15 mL), AgNO<sub>3</sub> (0.015 g), and glucose (0.1 g) was stirred for 30 min. The yellow-brown dispersion was then transferred to a 100 mL Teflon vessel, which was sealed, heated at a rate of 3 °C min<sup>-1</sup> to 120 °C, and maintained at this temperature for 24 h. It was then allowed to cool naturally to room temperature. The obtained black rGO hydrogel was completely immersed in ultrapure water (3×200 mL) to remove residual glucose and then freeze-dried for 48 h. Finally, the G-Ag aerogel was obtained by annealing at 700 °C for 3 h under H<sub>2</sub>/Ar (5:95, v/v) atmosphere, attained at a heating rate of 5 °C min<sup>-1</sup>.

#### Characterization

X-ray diffraction (XRD) patterns were measured on a powder X-ray diffractometer (Miniflex 600, Rigaku) employing Cu<sub>ka</sub> radiation ( $\lambda =$ 0.154 nm). Raman spectra were collected on a Raman spectrometer (Xplora, Horiba) at a laser wavelength of 532 nm. X-ray photoelectron spectroscopy (XPS) measurements were conducted with an XPS microprobe system (Quantum 2000, Physical Electronics). Nitrogen adsorption and desorption isotherms were measured on a surface area and porosity analyzer (BET, ASAP-2020, Micromeritics) using the Brunauer-Emmett-Teller (BET) method. Powder electrical conductivity was measured with a four-point probe powder resistivity meter (SZT-D, Suzhou Jingge Electronics Co., Ltd.) at a pressure of 2.0 MPa. The contents of Ag in G-Ag aerogels were measured by inductively coupled plasma-atomic emission spectrometry (ICP, NCS Testing Technology, Plasma1000). SEM and EDS mapping images were obtained by means of a scanning electron microscope (SEM, S-4800, Hitachi) equipped with an energydispersive spectrometry accessory (EDS, 7593-H, Oxford Instruments). TEM images were obtained with a transmission electron microscope (TEM, JEM-2100, JEOL). To characterize electrodes after Li deposition, they were removed from cells after a certain number of cycles, carefully washed three times with dimethyl carbonate (DMC), and allowed to dry naturally in an Ar-filled glove box.

#### **Electrochemical measurements**

CR-2016-type coin cells were assembled for electrochemical tests, and 1 m LiPF<sub>6</sub> in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1, v/v) + 5 wt % vinylene carbonate (VC) was used as the electrolyte (80  $\mu$ L). The G-Ag aerogel was cut and compressed into a disc-shaped electrode of diameter 12 mm, thickness around 170  $\mu$ m (Figure S1), and mass approximately 3.7 mg cm<sup>-2</sup>, and directly used as a working electrode. Li foil (diameter 12 mm, thickness 1 mm) was used as the counter and reference electrode. All batteries were first activated between 0.01 V and 1.5 V at 0.5 mA cm<sup>-2</sup> to remove contaminants and to form a stable SEI on the electrode surface. For cycling tests, a fixed amount of Li was plated on the G-Ag aerogel and then stripped away at up to 1.5 V at a given area current density (0.5 or 1.0 mA cm<sup>-2</sup>).

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### **Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** Ag nanoparticles • graphene • Li metal anode • lithiophilicity • mesoporous materials

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