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Layered Ag-graphene films synthesized by Gamma ray irradiation for stable lithium metal anodes in carbonate-based electrolytes

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ABSTRACT

Lithium metal batteries are considered as high energy density battery systems with very promising prospects and have been widely studied. However, The uncontrollable plating/stripping behavior, infinite volume change and dendrites formation of lithium metal anode restrict the application. The uncontrolled nucleation of lithium caused by the nonuniform multi-physical field distributions, can lead to the undesirable lithium deposition. Herein, a graphene composite uniformly loaded with Ag nano-particles (Ag NPs) is prepared through a facile Gamma ray irradiation method and assembled into self-supported film with layered structure (Ag-rGO film). When such film is used as a lithium metal anode host, the uncontrolled deposition is converted into a highly nucleation-induced process. On one hand, the Ag NPs distributed between the interlayers of graphene can preferentially induce lithium nucleation and enable uniform deposition morphology of lithium between interlayers. On the other hand, the stable layered graphene structure can accommodate volume change, stabilize the interface between anode and electrolyte and inhibit dendrites formation. Therefore, the layered Ag-rGO film as anode host can reach a high Coulombic efficiency over 93.3% for 200 cycle (786 h) at a current density of 1 mA cm⁻² for 2 mAh cm⁻¹ in carbonate-based electrolyte. This work proposes a facile Gamma ray irradiation method to prepare metal/3D-skeleton structure as lithium anode host and demonstrates the potential to regulate the lithium metal deposition behaviors via manipulating the distribution of lithiophilic metal (e.g. Ag) in 3D frameworks. This may offer a practicable thinking for the subsequent design of the lithium metal anode

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1. Introduction

Lithium-ion batteries (LIBs) have been widely applied in many aspects such as portable electronics, electric vehicles, energy storage grids and so on due to its high energy density and long cycle life. Nevertheless, with the exceeding development of technology and lifestyle, the traditional LIBs are unable to keep pace with the energy density demand of building a cleaner and low carbon society [1]. Therefore, the research and development of the next generation secondary battery with higher energy and power density are urgently needed [2]. Lithium metal with exceedingly high specific capacity (3860 mAh g^{-1}) and the most negative electrode potential (-3.04 V vs SHE) [3] is thought to be the ideal anode material. Furthermore, Li-S (theoretical specific capacity of 2600 Wh kg⁻¹) and Li-O₂ battery (theoretical specific capacity of 3500 Wh kg⁻¹) [4] which use lithium free compound cathode paired with lithium metal anode are typical high energy density systems with promising future [5,6].

However, different from the LIBs in which lithium ions are reversibly intercalated/deintercalated into graphite and oxides as a host electrode, the lithium plating/stripping reaction for lithium batteries is a conversion-pattern hostless process, therefore the volume change of anode is infinite during cycling. Moreover, the unstable deposition of lithium metal anode can cause the generation of "dead" lithium and the destruction of solid electrolyte

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interphase (SEI), eventually leading to low Coulombic efficiency. The uncontrollable plating/stripping behavior will also induce dendrite growth which could pierce the separator and lead to short circuit [4]. It can eventually result in the thermal runaway and a risk of explosion. Due to the unparalleled great temptation in energy density and the complexity of solving the problem restricted by the reversibility and safety, the application of lithium metal anode has always been regarded as the "Holy Grail" in the field of secondary batteries.

The growth of lithium metal is a multi-physical coupling process, which is affected by lithium ion diffusion, electric field distribution, current density distribution, temperature, etc. According to the traditional thermodynamic point, the nucleation of lithium can be depicted by Heterogeneous Nucleation Model established by Elyet et al. through thermodynamic and kinetic simulations [3,7,8]. The complex heterogeneous nucleation can be divided into different regimes. Initially, the embryos are thermodynamically unstable and tend to redissolve into electrolytes in the nucleation suppression regime. After some fluctuations of the multi-physics fields, the thermodynamically favored embryos continue to grow during a long incubation time regime. Once exceed the critical overpotential, lithium with critical kinetic radius rapidly nucleates with the increase of overpotential during the short incubation time regime which is beneficial to the narrow size distribution of embryos. Finally, the nuclei with thermodynamical and kinetical stability grow into the same size with constant growth rate during the early and subsequently later growth regimes. It should be pointed out during the short incubation time regime, the nucleation of lithium needs to overcome certain nucleation barrier, requiring a critical overpotential as the driving force. The presence of such an overpotential can lead to the formation of local charge field at nucleation sites and uneven distribution of lithium ions which can make for uneven deposition of lithium [9]. As discussed in previous studies, the nucleation morphology is also highly correlated to critical overpotential. The nucleation radius is the reciprocal of the nucleation overpotential, and the nucleation density is proportional to the cubic of the nucleation overpotential [10]. Obviously, larger overpotential leads to higher nucleation radius and more lithium crystal nuclei, which means larger specific surface area and more deposition sites. It would consume more electrolyte to form SEI membrane and may lead to the generation of whiskery dendrites. Hence, reducing and even eliminating nucleation overpotential is of great benefit to uniform lithium metal deposition morphology.

Previously, many researchers have explored the nucleation overpotential during the lithium metal deposition. Cui and his collaborators [11] proposed that there is no nucleation overpotential when lithium is deposited on lithiophilic metal substrates such as Au, Ag, Zn, Mg, etc. This can be explained by the formation of solid solution buffer layer due to the definite solubility of the metal substrate in lithium metal. It can reduce the nucleation energy barrier, which will decrease and even eliminate the nucleation overpotential. Lower overpotential facilitates uniform deposition of lithium metal without dendrite and "dead" lithium. Besides, lithium probably tends to preferably deposit at more lithiophilic sites with lower nucleation energy barrier, which indicates the potential to regulate the deposition behaviors of lithium by introducing different lithiophilic metal [12]. However, due to the uneven distribution of current density and electric field, the anode structure needs to be further modified.

As a result, designing stable deposition matrix material as host is also an effective strategy to alleviate volume change, promote the uniform deposition of lithium and restrain the growth of dendrites for lithium metal anode [13,14]. In this regard, porous skeleton materials with excellent electron conductivity and high specific surface are particularly recommended [15,16]. Intuitively, the porous skeleton provides space to accommodate lithium metal and inhibits the volume change during cycling. Besides, owing to their high specific surface area, it can enable relatively low local current density and thus promote the uniform deposition of lithium. Moreover, among various kinds of materials, the 3D carbon materials are considered as the most explored matrix for lithium deposition due to its good electronic conductivity, high structural universality and excellent chemical stability [17–20].

The integration of lithiophilic metal and 3D carbon matrix as lithium metal host thus is a promising approach towards the pursuit of high-performance lithium metal anode [21-23]. For instance, Zhang et al. [24] designed a sandwich composite anode consisting of gold nanoparticles pillared reduced graphene oxide (rGO). Because of the utilization of the gold nanoparticles which can preferentially induce lithium nucleation, the normally uncontrolled lithium deposition process was refined into a highly nucleation-guided process. Meanwhile, the sandwich structure provides a stable framework with stable solid electrolyte interface. Zhao et al. [25] prepared a rationally designed three-dimensional graphene/Ag aerogel (3D G-Ag aerogel) via hydrothermal synthesis as lithium deposition substrate. The Ag particles can effectively lower the energy barrier of lithium nucleation and regulates uniform lithium deposition behavior. Besides, the highly flexible and conductive three-dimensional porous structure can accommodate the deposited lithium and ensure the integrity of the conductive network during cycle.

Gamma ray irradiation in aqueous solutions dispense with harsh reaction conditions (e.g. high temperature and high pressure) provides a clean alternative to the existing methods. Some previous studies have been launched on Gamma ray method [26]. The energy deposition in this process is not selective and the reaction process is fast so that it is hard to form the agglomeration of metal nanoparticles. Therefore, the composite nanomaterials obtained by Gamma ray irradiation have the advantages of uniform dispersion of metal particles with small particle size as well as strong loading force. Simultaneously, Gamma ray irradiation is a synthetic method that can be used as mass production and it can be carried out under mild conditions using the irradiation allowance of industrial production. Overall, it is a facile production method that can be extensively applied.

Herein, as schemed Fig. 1, assisted with Gamma ray irradiation, on-site reduction of Ag⁺ and homogeneous deposition of Ag NPs were achieved straightforwardly while the layered graphene oxide (GO) nanosheets were also partly reduced in this process. The Ag NPs can be facilely embedded within graphene sheets through in situ reduction reaction. The resulting composites were further assembled into a self-supporting film with high structural integrity through vacuum filtration. The self-supporting film has the layered structures parallel to the separator to maintain the stability of the interface between electrolyte and anode. The Ag NPs were found to reduce the nucleation overpotential and induce uniform deposition of lithium metal between graphene interlayers while the layered graphene sheets can reduce local current density and inhabit volume expansion during cycling. Owing to these merits, the layered Ag-rGO film exhibits a high CE over 93.3% for at least 200 cycles with a high capacity of 2 mA h cm⁻² in carbonate-based electrolyte.

2. Experimental

2.1. Preparation of Ag-rGO nanosheets

2 g graphene oxide powder (GO 1211, Ashine, Shanghai) was dispersed in 190 mL ultrapure water, towards which 0.34 g AgNO₃ and 10 mL isopropanol were added. After being ultrasonicated for



Fig. 1. Schematic diagram of Gamma ray irradiation and procedure for obtaining the layered Ag-rGO film.

2 h, the mixture was bubbled with argon for 30 min to remove the dissolved oxygen. The dispersion was then sealed and irradiated with ⁶⁰Co Gamma ray at room temperature with a total dose of 20 kGy. The obtained product was washed by water and ethanol for three times respectively and collected by centrifuge, and then dried in air at 60 $^{\circ}$ C for 24 h to obtain the final Ag-rGO composite powder.

2.2. Assembly of Ag-rGO nanosheets into layered films

50 mg Ag-rGO powder was dispersed in 200 mL ultrapure water by ultrasonication for 2 h; after that, the suspension was subjected to vacuum filtration to yield the layered film with a diameter of 50 mm. The Ag-rGO film was cut into round discs with diameter of 12 mm, which then were annealed under H₂/Ar (5:95, by volume) atmosphere at 700 °C for 3 h, with a heating rate of 5 °C min⁻¹.

2.3. Materials and electrochemical characterization

X-ray diffractometer (XRD, Miniflex 600, Rigaku) was used to measure the XRD patterns, employing $Cu_{K\alpha}$ radiation $(\lambda = 0.154 \text{ nm})$. Scanning electron microscopy (SEM, Zeiss Gemini SEM 500) with Energy Dispersive X-Ray Spectroscopy (EDX, Ultim extreme, Oxford) and transmission electron microscopy (TEM, Tecnai F30 TWIN, FEI) was used to obtain the morphology, microstructure and element distribution. Pore size distributions by nitrogen adsorption and desorption isotherms were measured on a Brunner - Emmet - Teller analyzer (BET, ASAP-2020, Micromeritics). X-ray photoelectron spectroscopy (XPS) was conducted on Thermo Scientific K-Alpha. The contents of Ag in different samples were tested by inductively coupled plasma-atomic emission spectrometry (ICP, Plasma1000, NCS Testing Technology). Coin cells (CR2032) were assembled with Celgard 2500 separators in a glove box (Ar, $O_2 < 0.5$ ppm, $H_2O < 0.5$ ppm). The carbonate-based electrolyte is 1 M LiPF₆ dissolved in ethylene carbonate/dimethyl carbonate (EC/DEC, 1:1, by volume) with 5 wt% vinylene carbonate (VC). About 75 µL electrolyte was added into each cell. The electrochemical properties were characterized by a galvanostatic charge/ discharge protocols on a Wuhan Land Battery Tester. All cells were cycled between 0.01 and 1 V at 0.5 mA cm^{-2} for three times to stabilize the SEI formation before test. Electrochemical impedance spectroscopy (EIS) measurements were conducted from 10 mHz to 100 kH on Solartron 1287/1260.

3. Results and discussion

The XRD pattern of the as-synthesized Ag-rGO composite is shown in Fig. 2(a). The obvious crystalline peaks at 38.12° , 44.23° , 64.42° , 77.47° and 81.54° can be assigned to the (111), (200), (220), (311), and (222) planes of metallic Ag. The diffraction

peak at 10.88° corresponds to (002) plane of GO before Gamma ray treatment and the wide characteristic peak centered at 26.58° can be assigned to both crystalline and amorphous phases of graphite in the Ag-rGO. The element mapping image (Fig. 2(b)) shows that Ag NPs are uniformly distributed between the graphene sheets. The surface morphology (Fig. 2(c) and (d)) indicates that the graphene sheets are tightly interconnected with each other and the Ag NPs are uniformly embedded or encapsulated within the layered graphene sheets. Fig. 2(d) reveals that the diameter of Ag NPs loaded within the graphene sheets ranges from 20 nm to 50 nm. (Fig. S1) During the Gamma ray irradiation process, the water is decomposed into H•, eaq, and OH•, The first two species are very reactive species with negative reduction potentials of E_0 $(H^+/H_{\bullet}) = -2.3$ V vs. NHE, and $E_0 (H_2O/e_{a0}) = -2.87$ V vs. NHE, respectively [27]. They can easily reduce solvated Ag⁺ to zerovalence. Using secondary alcohols as OH• radical scavengers, more reducing species are generated and a highly reducing environment is promoted. This environment is beneficial to the reduction of Ag⁺ precursor, promoting the formation of crystal nuclei and the growth of Ag NPs. Moreover, due to the quick and non-selective reduction process under Gamma ray irradiation, the Ag atoms tend to form Ag NPs in narrow size distribution without aggregation. The content of Ag NPs determined by ICP is about 6.82%. The concentration of Ag NPs could also be controlled by adjusting the dose of irradiation and the concentration of precursor AgNO₃. (Table S1)

The TEM diagram (Fig. 3(a) and (b)) shows that Ag NPs are tightly embedded or encapsulated within the graphene sheets. In the precursor solution, Ag ions tend to coordinate with negatively charged oxygen-containing functional groups on GO sheets. Under high-energy Gamma ray irradiation, the co-reduction of functional groups of GO and Ag⁺ will be initiated by H• and e_{eq} [28], forming Ag-rGO composite with strong loading force [29]. Fig. 3(c) shows the corresponding selected area electron diffraction (SAED) pattern, the symmetrical dots can be indexed to Ag nanocrystals and the diffraction ring may be ascribed to graphene. A highresolution transmission electron microscopy (HRTEM) image (Fig. 3(d)) displays that the lattice fringe is about 0.24 nm, consist with the (111) planes reflection of cubic Ag. All of the above manifest that the Gamma ray irradiation method is easy to obtain the Ag-rGO composite in which Ag NPs are uniformly embedded within the graphene sheets. This Ag-rGO composite prepared by Gamma ray irradiation has the advantages of narrow Ag particles size (about 20 to 50 nm), uniform particles distribution and strong loading force. The uniformly dispersed Ag NPs within graphene sheets can reduce the overpotential and induce the deposition of lithium between the interlayers of graphene so as to promote uniform deposition and inhibit the volume expansion of lithium during deposition.

The self-supporting Ag-rGO film with multilayer structure is obtained by vacuum filtration process of Ag-rGO composite. Fig. 4(-a-c) show the cross-sectional SEM image and element mappings of



Fig. 2. (a) XRD pattern of Ag-rGO and GO. (b) Optical image and elemental mappings of the Ag-rGO film. (c,d) Surface SEM images of Ag-rGO film.



Fig. 3. (a) TEM image of Ag-rGO composite. TEM image (b) and corresponding SAED pattern (c) of a single Ag NP embedded within graphene. (d) HRTEM image of a single Ag NP.

Ag-rGO film. It can be identified that the graphene sheets are stacked with each other, forming a layered structure with Ag NPs evenly embedded within them. The elemental mappings also show that Ag NPs are uniformly distributed between the Ag-rGO film. To further observe the distribution of Ag NPs between graphene sheets, a top to bottom linear element scanning was carried out. It can be seen from the vertical distribution diagram of Ag element (Fig. 4(d)) that a higher Ag concentration at the bottom of Ag-rGO film is obtained. It could be attributed to the effect of water flow during vacuum filtration. During the Gamma ray irradiation



Fig. 4. Cross-sectional SEM image (a) and corresponding elements mappings (b and c) of Ag-rGO film. (d) Vertical distribution diagram of Ag element.

preparation process, a large proportion of Ag NPs are loaded within graphene sheets, while some excess Ag NPs are reduced and suspended in solution. During the subsequent process of extraction, Ag NPs suspended in the solution will roll to the bottom under the influence of water flow, forming a higher concentration of Ag NPs, while Ag NPs loaded on the graphene layers will be uniformly distributed within the Ag-rGO film. The induction effect of Ag NPs could induce the preferred deposition of lithium, so that lithium will deposit between graphene sheets and preferentially deposit at the bottom with higher concentration. This kind of preferential interlayer deposition behavior is conducive to inhibiting the volume expansion of lithium, maximizing the utilization of layered host structure, maintaining the stability of the interface between lithium metal and electrolyte, and improving the cycling stability of lithium metal anode. The absorption desorption curve and pore diameter distribution (Fig. S2) acquired from BET test confirm that the load of Ag NPs improves the porosity and specific surface area of the layered graphene sheets. This structure can reduce local current density and provide more space to accommodate lithium deposition. However, the Ag-rGO film is still dominated by micropores, corresponding to the layered structure shown in SEM diagram of the section (Fig. 4(a)). The structure is not a loose and porous structure, but a stacked layers structure, which can construct a great conductive network, maintain the stability of the structure, improve the interface stability of anode and electrolyte, and improve its long cycle performance.

By characterization of XPS, chemical composition and valence state of the Ag-rGO composite were studied. The Ag 3*d* spectrogram (Fig. 5(a)) can be decomposed into two peaks at 368.6 eV and 374.6 eV, corresponding to Ag $3d_{5/2}$ and Ag $3d_{3/2}$ [30], respectively. This attests the formation of Ag NPs. In the process of highenergy Gamma ray irradiation, the oxygen-containing functional groups of graphene oxide will be reduced simultaneously as the reduction of Ag⁺. However, the graphene after irradiation treatment can still have some oxygen-containing functional groups, so an annealing treatment was introduced to further deoxidize the graphene for higher electronic conduction. As is shown in the C1s diagram before and after irradiation (Fig. 5(b) and (c)), the peaks of C1s can be attributed to C-C (284.8 eV), C-O (287 eV) and C = O (288 eV) bonds respectively [31]. According to the calculation of peak area, the relative content of oxygen-containing bond and C-C bond after irradiation is about 1.08, which is lower than that of 1.41 before irradiation. This demonstrates that partial reduction of the oxygen-containing functional groups certainly occurred during irradiation. After further annealing treatment in H₂/Ar atmosphere, C1s diagram (Fig. 5(d)) shows that the relative content of oxygen-containing bond and C-C bond is further decreased to 0.69. The deep deoxidation of graphene is particularly important to polish graphene's conductive properties. A good conductive framework is beneficial to connect the lithium deposited in the graphene sheets and reduce the generation of "dead" lithium. To confirm this result, the Raman spectroscopy of GO and Ag-rGO after irradiation and after further annealing treatment was also obtained (Fig. S3). The two broad peak at around 1348 cm⁻¹ and 1591 cm⁻¹ can be ascribed to D band (defect sites and disorders) and G band the (graphite band) of carbon materials respectively [32]. The I_D/I_G ratio of GO is approximate to the Ag-rGO film (0.98) after irradiation, indicating that the irradiation process didn't add graphitic domains but just reduced partial oxygencontaining functional groups of GO. However, the I_D/I_G ratio was increased to 0.89 through annealing process which means the crystallinity of Ag-rGO film was enhanced. The generation of new graphitic domains after annealing is corresponding to the deep deoxidation as shown is XPS analysis which is in favor of constructing a good conductive network.

To verify whether the layered Ag-rGO film with evenly loaded Ag NPs and relatively higher Ag NPs concentration at the bottom can induce uniform deposition of lithium between graphene layers, The Ag-rGO film were assembled with Li foil to deposit lithium on it. Fig. 6(a-c) show the morphology of the Ag-rGO after the deposition of 2 mAh cm⁻² lithium. As can be seen from Fig. 6(c), continuous and compact lithium deposition layer is observed at the



Fig. 5. (a) Curve fit of Ag 3d XPS spectrum of Ag-rGO composite. Curve fit of C 1 s XPS spectrum of GO (b), Ag-rGO (after irradiation) (c) and Ag-rGO (after annealing) (d).



Fig. 6. Optical images of Ag-rGO film (a) and rGO film (d) after plating with lithium of 2 mAh cm⁻². Surface (b) and cross-sectional (c) SEM images of Ag-rGO film after plating with lithium of 2 mAh cm⁻².

bottom of film, while the layered structure of upper layers is still maintained. This indicates that high concentration of Ag NPs at the bottom of the anode induces the preferred deposition of lithium to some extent. The energy barrier of lithium deposition on the formed lithium metal is lower and lithium tends to grow on the existing lithium base rather than form new nuclei. Therefore, lithium tends to deposits along the graphene sheets from the bottom up under the inductive effect of Ag NPs and preferred deposited lithium. The surface morphology (Fig. 6(b)) also represents that the surface is flat without obvious accumulation of lithium after the deposition of 2 mAh cm⁻² lithium. This shows that lithium preferentially deposits between the graphene sheets under the induction of Ag NPs, which is similar to the insertion of lithium ions between graphite layers. In addition, the interlayer deposition can stabilize the interface between the anode surface and electrolyte, as well as maintain stable structure in the process of long cycle, so as to improve the performance of Ag-rGO film. Take rGO film without Ag as contrast (Fig. 6(f)), after the deposition of 2 mAh cm⁻² lithium, lithium accumulates at the top of graphene layers with obvious stratification between whisker lithium and graphene base. Represented by surface morphology (Fig. 6(e)), the surface deposition will generate local accumulation and whisker structure, readily leading to the lithium dendrite and "dead" lithium. Due to Li⁺ transfer resistance between graphene sheets, Li⁺ will not preferentially enter the interlayers of rGO film and plate between graphene sheets, leading to the local accumulation at the top of rGO film which is similar to the deposition behavior on Cu foil. It is also obvious from the optical picture (Fig. 6(a) and (d)) that local lithium accumulation was formed on the surface of rGO, while the Ag-rGO surface remained uniform and flat. This manifests that the preferable deposition behavior induced by Ag NPs does help to promote uniform deposition of lithium between interlayers. The XPS test was also conducted to Ag-rGO and rGO film which have been pre-cycled for three times to form SEI membrane and deposited 2 mAh cm^{-2} of lithium. (Fig. S4). As for F 1 s spectrum (Fig. S4a and b), the two peaks located at about 688.2 and 685 eV could be assigned to C-F bond-containing compound (derived from the polymerized C–F molecule) and LiF, respectively. Obviously, more LiF can be found in Ag-rGO film which means superior SEI membrane containing more LiF was constructed. The C 1 s spectrum exhibited the three peaks centered at 284.8, 287, and 290 eV which are corresponding to C-C, C-H, and C = O functional group, respectively. It also demonstrated SEI membrane of Ag-rGO film contains more oxygen-containing functional groups which is related to more flexible SEI membrane. Thanks to the uniform deposition of lithium between interlayers, the interface between Ag-rGO film and electrolyte was stabilized and better SEI with more LiF and better flexibility was constructed.

The induction effect of Ag combining with layered structure of graphene sheets shows great strengths in promoting uniform deposition between layered structure. This deposition behavior can maximize the utilization of the layered structure to accommodate volume expand, inhabit dendrite growth and stabilize the interface between electrolyte and anode. Besides, the distinguishing Ag NPs distribution shows the potential to regulate prior deposition sites of lithium, further demonstrating the induction effect of Ag NPs.

In order to test whether the layered Ag-rGO film prepared by Gamma ray irradiation as lithium metal anode host can exhibit superior electrochemical performance, coin cells are tested with layered Ag-rGO films as working electrodes, Li foils as counter electrodes and reference electrodes as well as carbonate-based electrolyte. It is known that nucleation overpotential is an important parameter to evaluate the electrochemical performance of lithium plating/stripping process. Large overpotential is likely to contribute to uneven deposition of lithium and be detrimental to the reversibility [33]. Fig. 7 displays the initial discharge voltage profile of different anodes. Cu foil as the reference substance showed a 170 mV overpotential at the beginning, while the rGO showed a 140 mV overpotential. However, Ag-rGO film did not show obvious overpotential because lithiophilic Ag NPs can lower the nucleation barrier so that the nucleation overpotential can be effectively reduced. Larger overpotential means higher nucleation radius and more lithium crystal nuclei, which contributes to larger specific surface area and more deposition sites [10]. It can consume much more electrolyte to form SEI membrane and easily lead to the generation of whiskery dendrites. Visibly, the load of Ag NPs can effectively eliminate the nucleation overpotential of lithium plating. Ag-rGO film with almost zero overpotential is conducive to the uniform deposition of lithium and improved cycle performance.

Further on, to verify whether Ag NPs could promote the uniform plating of lithium and improve cycle performance, preceding coin cells were cycled by galvanostatic method. Fig. 8(a) displays the Coulombic efficiency (CE) of different anodes cycled at 1 mA cm⁻² current density for 2 mAh cm⁻² deposition capacity. Ag-rGO film showed excellent long cycle performance, maintaining a CE over 93.3% under 200 cycles, while the CE of Cu foil rapidly decreased after 50 cycles. rGO film also did not show desired performance, whose CE rapidly decreased to failure after 70 cycles. These differences might be rooted in the continuous consumption of recyclable lithium ions for the formation of SEI and "dead" lithium, which is highly correlated with the morphology of lithium deposits shown in Fig. 6. Because of the absence of Ag particles, Li mainly deposited on the surface of rGO film and did not enter the interlayers of graphene, so it could not give play to the advantages of layered structure. This nonuniform accumulation and whisker structure of lithium can result in relatively larger lithium/electrolyte contact, inducing higher SEI consumption. When whisker lithium is stripped, the infinite volume changes further aggravate the morphology and even leave "dead" lithium. All of this dramatically impair the CE of rGO film and Cu foil. On the contrary, the lithium was plating between the graphene sheets induced by Ag NPs so that the CEs was improved. This is probably because the deposition behavior could reduce the lithium/electrolyte contact area, facilitate uniform deposition of lithium and inhibit the formation of "dead" lithium. Cycle performance at higher current density (2 mA cm^{-2}) and higher deposition capacity (4mAh cm^{-2}) was also shown in Fig. 8(c). Ag-rGO film can still maintain a CE of more than 94% after 100 cycles, while rGO and Cu foil failed rapidly after 30



Fig. 7. Galvanostatic discharge voltage profiles of different anodes during the initial lithium deposition at 1 mA cm⁻².



Fig. 8. Coulombic efficiencies of Ag-rGO film, rGO film and Cu foil at (a) 1 mA cm⁻² for 2 mAh cm⁻² and (b) 2 mA cm⁻² for 4 mAh cm⁻². Typical voltage profiles of (c) the Ag-rGO film and (d) the rGO film at 1 mA cm⁻² for 2 mAh cm⁻². (e) Nyquist plots of Ag-rGO film and Cu foil in the 10th and 60th cycles.

and 10 cycles respectively. This is because the higher specific surface area of layered structure can reduce the local current density, which can significantly improve cycle performance under higher current density. Beyond that, the layered graphene structure provides sufficient storage space to plate lithium and inhabits volume expansion, increasing the performance of Ag-rGO under greater deposition capacity. Cycling performance test in other different charging/discharging conditions were also conducted (Fig. S5). Ag-rGO film also exhibited better performance. Due to the uniform deposition behavior induced by Ag NPs and stable layered structure of graphene, Ag-rGO film reveals significantly improved cycle performance with high specific capacity of 848 mAh g⁻¹ and 1396 mAh g⁻¹ in carbonate-based electrolyte (Table S2).

Fig. 8(c and d) displays the voltage profiles of different anodes. The rGO film shows obvious voltage fluctuation after 80 cycles. This can be ascribed to the local accumulation of lithium metal on the surface of rGO film, leading to irreversible plating/stripping and local dendrite formation which could result in short circuit. Ag-rGO film were still able to keep commendable reversible plating/stripping even after 200 cycles. The uniform deposition between layered graphene sheets can be analogous to the intercalate/deintercalate behavior of graphite which can make for long cycling life. The EIS tests were conducted to further study the interface characteristic of different anodes. The Nyquist plots (Fig. 8(e)) contain two semicircles, which can be interpreted using two series-wound equivalent analogs of retractor- capacitor (RC) circuits in series (Fig. S6). The R_{SEI} in the first part can be assigned to transport impedance of lithium ions in the SEI film, and the semicircle diameter is proportional to the migration impedance of lithium ions in the SEI film. In the 10th cycle, the semicircle diameter of Ag-rGO and rGO are close to each other, valuing 102.7 Ω and 107 Ω respectively. But after the 60th cycle, both of the SEI film impedance increased to 161.3 Ω and 168.2 Ω , respectively. This indicates that as the charging-discharging process, the SEI membrane gradually thickened, increasing the migration resistance of lithium ions in the SEI membrane. The R_{ct} in the second part represents the charge transfer process. The diameter of the

semicircle is proportional to the electron transfer impedance of anode. After the 10th cycle, the semicircle diameter of Ag-rGO and rGO are 76.42 Ω and 117.7 Ω respectively, indicating that the electron transfer impedance of rGO is significantly greater than Ag-rGO. This suggests that the Ag-rGO has a better electronic conductive network, which is advantageous to the electronic conduction. After 60th cycle, The charge transfer impedance of rGO rapidly increased to 610.4 Ω , much larger than the 239.3 Ω of Ag-rGO. This is because lithium accumulated on the surface of rGO film, producing large amounts of "dead" lithium after the repeated cycle, which can hamper the electronic conduction. On the contrary, lithium is mainly deposited between the conductive framework of graphene in Ag-rGO film, so as to effectively reduce the electron transfer impedance. The construct of a good conductive network is helpful to reduce current density and connect the deposited lithium, so as to eliminate the formation of "dead" lithium. The better conductive network constructed by layered graphene sheets and Ag NPs effectively promotes the reversible plating/stripping of lithium and reduces the electron and ion transfer impedance.

In order to verify whether the Ag-rGO film can maintain the layered structure after cycling, the morphology of the Ag-rGO and rGO films at stripping stage after cycling for 60 cycles was observed by SEM as shown in Fig. 9. The Ag-rGO can still maintain layered structure, without obvious generation of "dead" lithium on the surface. In contrast, there exists a thick layer with foamy morphology coating on the surface of rGO film. It might be due to the "dead" lithium cannot be stripped again, which will cause the low CE. In addition, the foamy "dead" lithium cannot form a good conductive network, so that it will hinder the electronic transfer of anode and increase the charge transfer impedance, which is consistent with the conclusion of the EIS analysis (Fig. 8(e)). This manifests that Ag-rGO film is able to maintain the layered structure without obvious "dead" lithium after repeating cycles. The great stability of layered Ag-rGO structure during reduplicative plating/stripping of lithium is crucial to play its role in promoting uniform deposition after long cycle.



Fig. 9. Surface and cross-sectional SEM images of (a and b) Ag-rGO and (c and d) rGO after 60th cycles.

We also prepared full cell with LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ as cathode to study the compatibility of Ag-rGO film with high-voltage cathodes. Fig. S7a and b show that the full cell maintained an 87.9% discharge capacity after 200 cycles at 1C with a reversible discharge capacity of 131mAh g⁻¹, with a cut-off voltage range from 2.75 V to 4.3 V, while the full cells matched with rGO film and Cu foil exhibited rapid decline of capacity after only 100 cycles (Fig. S7c). The uniform deposition of lithium between layered graphene sheets is similar to the intercalate/deintercalate behavior of graphite interlayer which makes for the high capacity retention matching with high-voltage cathodes. The great compatibility with high-voltage cathodes is beneficial to giving play to the high capacity characteristics of lithium metal anode.

4. Conclusion

In general, a kind of graphene material uniformly loaded with Ag NPs is prepared through a simple method of Gamma ray irradiation was obtained and the composites was assembled into a selfsupported layered film as lithium metal anode host. Thanks to the lithiophilic Ag NPs distributed between the interlayers, the nucleation energy barrier of lithium can be reduced, as well as the nucleation overpotential, which can induce uniform deposition morphology between interlayers. This deposition behavior can maintain the stability of layered structure and improve the stability of interface between Ag-rGO and electrolyte, beneficial to the stability of the SEI film, so as to reduce the consume of electrolyte caused by the SEI film damage. The good conductive framework constructed by graphene sheets can reduce current density, inhabit the generation of "dead" lithium and dendrites. The Ag-rGO film also exhibited the great stability during reduplicative plating/stripping. Therefore, the layered Ag-rGO film as lithium metal anode host showed a high CE over 93.3% after 200 cycle at a current density of 1 mA cm⁻² for 2mAh cm⁻² in carbonate-based electrolyte.

This work demonstrates the potential of using Gamma ray irradiation to prepare metal/3D-skeleton structure as lithium anode. This is a facile production method under mild condition, which can be extended to the preparation of a variety of metal composite materials. Besides, the preferential deposition of lithium under the inductive effect of high concentration of lithiophilic Ag NPs verified the potential for regulating the deposition sites of lithium via controlling the distribution of lithiophilic metal in a three-dimensional framework. This offers a practicable thinking for the subsequent design of the lithium metal anode.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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