Interlayer Lithium Plating in Au Nanoparticles Pillared Reduced Graphene Oxide for Lithium Metal Anodes

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Lithium metal anodes suffer from serious safety issues and rapid capacity fade because of nonideal plating/striping behaviors. Lithium nucleation on undesired positions usually results from nonuniform multiphysical field distributions and the dynamically changing interface thermodynamics. In this study, a sandwich composite anode consisting of gold nanoparticles pillared reduced graphene oxide (rGO) is designed. Because gold nanoparticles preferentially induce lithium nucleation, the typically uncontrolled lithium deposition process becomes a highly nucleation-guided process. Because the sandwich structure of the Au-pillared rGO provides a stable anode morphology with cycling and stabilizes the solid electrolyte interface layer, the Au-pillared rGO delivers a high Coulombic efficiency of up to 98% for at least 200 cycles for 1600 h. Using this pillared structure, an interlayer plating process is revealed in rGO-sandwiched anodes, which differ from either conventional metallic anodes or intercalation anodes. The Au-pillared design bridges the gap between metal and intercalation anodes, and provides a novel strategy to improve the efficiencies and cyclability of lithium anodes.

1. Introduction

Lithium metal anodes have recently captured increasing attentions because of lithium's high capacity of 3860 mA h g⁻¹ and low electrode potentials.¹⁻⁴ However, during cycling, lithium plating and stripping is usually nonideal, resulting in dendrite growth and serious safety issues. This is compounded by the fact that because of its high activity, lithium reacts with electrolyte and forms a surface electrolyte interphase (SEI). As illustrated in Figure 1a, the morphological change of lithium during plating/striping leads to the SEI accumulation and “dead lithium,” which is manifested by a low Coulombic efficiency (CE).⁵ Realization of practical lithium anodes will require overcoming all these challenges.

Dendrite growth is governed by the lithium/electrolyte interphase properties and also influenced by the nonuniform distributions of multiphysical fields such as lithium-ion (Li-ion) concentration, local potential, local current, and so on.⁶ Classic thermodynamics indicates that the interfacial energy differences among lithium, electrolyte, and host materials govern the nucleation and growth of metallic lithium. Previous studies reported that the interface energies could be adjusted by electrolyte additives as a path to suppress lithium dendrite growth.⁷⁻¹⁴ Cui and co-workers studied the overpotentials of various materials (Au, Cu, Ni, Pt, Al, and so on) on lithium nucleation and concluded that the formation of a solid solution with lithium would help lithium nucleation because of the reduced lithium/host interfacial energy (see Figure S1a in the Supporting Information).¹⁵ Studies on how to tune the
interface energy provide an effective approach to design a better lithium anode. However, as multiphysical field distributions and local interface properties simultaneously govern lithium plating/stripping, both field distributions and interface energies need to be taken into account to further improve the performance of lithium metal anodes.

Empirical observations and simulations have revealed that lithium is usually deposited at electrode edges, separator/anode interfaces, or sharp protrusions. The onset of lithium dendrite has been correlated to the nonuniformity of electrode geometry and microstructure properties. Figure 1b–d provides examples of lithium plating in three reduced graphene oxide (rGO) electrodes that have a thin layer of gold coating on the top (Figure 1b), in the middle (Figure 1c), and at the bottom (Figure 1d) of the electrode. The spot-like lithium growth along the edges and top surface of all three samples indicates the nonuniform plating on the rGO anodes. Because the properties of rGO/electrolyte interfaces are almost homogeneous in the electrode, the preferential deposition on the top and edges results from the easy accessibility of Li-ions and enhanced electric fields, which are influenced by the geometric microstructures.

The nonuniform nucleation induced by structure has been studied via classic spherical cap and 2D nucleation models. First, high overpotentials could significantly reduce the critical radius (Figure S1b, Supporting Information). The spherical cap model may evolve into a 2D model, in which the critical radius decreases with the increase of substrate curvatures. Second, electric fields concentrate at sharp tips or regions of high curvatures. Many studies reported that the field concentration induces nonuniform growth of lithium. A variety of curvature distribution exist in conventional anodes that consist of particular host materials or porous scaffold. Under high-current densities or repeated cycling conditions, the electrode edges and highly curved tips along the separator/anode interface will become the hot spots for lithium plating. The resulting nonuniform lithium nucleation/growth put batteries in the danger of short circuits. Mitigating the nonuniform lithium plating is usually secured by operating batteries under mild conditions (such as low rates and appropriate temperatures). The three examples in Figure 1b–d show that lithium prefers to deposit where gold is positioned. It demonstrates that via appropriately designed composite structures, lithium dendrite formation may be significantly suppressed.

Here, we illustrate the potential of a gold nanoparticles (Au NPs) pillared rGO as the basis of a metallic lithium anode. The Au NPs pillared rGO (Au-rGO) has the general laminate structures parallel to the separator to modestly reduce the high curvature surface and avoid sharp protrusions. To reduce the
possibility of lithium plating at the surface, where there is easy accessibility of Li-ions, rGO is deliberately exposed at the electrode/separator interface because rGO has high nucleation energy barriers. Gold, which has a low barrier to lithium plating, is placed where lithium nucleation has low probability due to the difficult Li-ion transport. The lithium plating process is thus guided by the nucleation process and not local nonuniformities (such as Li-ion concentration and electric fields). In Au-rGO, lithium plating/stripping is significantly different as compared to simple rGO. The Au NPs induce lithium deposition between rGO sheets (where Au NPs are sandwiched). This plating mode superficially resembles Li-ion “intercalation” but of course is fundamentally quite different, as a metallic lithium strip instead of a single Li-ion layer is inserted between rGO sheets as shown in Figure 1e. We call this mode as interlayer lithium plating. This plating mechanism enables the minor morphological changes of SEI layers with cycling because the in-plane distortion of the anode structures is avoided and only the through-plane size expands or shrinks to accommodate lithium insertion and extraction. Because of these design advantages, Au-rGO electrode demonstrates a high CE of up to 98% for at least 200 cycles with a high capacity of 2 mA h cm$^{-2}$ for 1600 h, as compared to other previous studies,[29,34–36] which is superior to Cu-based and rGO-based lithium metal anodes in terms of both the CEs and cyclability.

2. Results and Discussion

Figure 2a,b shows the cross-section scanning electron microscopy (SEM) images of an rGO electrode. The rGO sheets are generally stacked in parallel. The slightly crumpled rGO layers exhibit some interlayer gaps, which perhaps facilitate Li-ion transport during cycling. Figure 2c illustrates the possible Li-ion diffusion pathway through the gaps and crevices of the stacked rGO layers. When Au NPs were introduced into the precursor graphene oxide (GO) suspension, the filtration-based stacking process led to a stacked GO film which was pillared by Au NPs. After treatment with hydrazine hydrate, GO was reduced, forming what we term Au-rGO. The SEM images in Figure 2d,e indicate that Au NPs were randomly distributed between the rGO sheets. Au NPs were also collected for further characterization by ultrasonication and filtration. The transmission electron microscope (TEM) images in Figure 2g,h and Figure S3 in the Supporting Information reveal that Au NPs are 10–20 nm in diameter. The lattice fringe of $\approx 0.235$ nm in Figure 2h is in agreement with the gold (111) planes spacing. Figure 2i presents the X-ray diffraction (XRD) patterns of the GO, rGO, and Au-rGO samples. GO presents a typical sharp diffraction peak at about 11°, corresponding to the (002) reflection peak of GO sheets.[37,38] The rGO sample shows a peak at $\approx 26°$ and lacks a GO peak, indicating the reduction of GO.[39]

![Figure 2. Cross-sectional SEM images of a,b) rGO and d,e) Au-rGO at varied magnifications (Au NPs have been colored yellow for easy of identification, see Figure S2 in the Supporting Information). Schematic illustrations of c) rGO and f) Au-rGO. g) TEM image of Au-rGO. h) HRTEM image of a single Au NP. i) XRD patterns of GO, rGO, and Au-rGO.](image-url)
The strong and sharp peaks from Au-rGO are indexed to gold (JCPDS Card No. 04–0784).

To test whether Au NPs could reduce the nonuniformity of lithium plating, we assembled Au NPs pillared rGO samples with lithium and cycled them using a capacity-limited protocol. Figure 3a,b shows cross-sectional SEM images of two Au-rGO samples which were plated with lithium to capacities of 0.25 and 2 mA h cm\(^{-2}\), respectively. It could be seen that as the capacity increased, the multilayered sheets were gradually filled with solid lithium and the interlayer gaps narrowed due to the out-of-plane expansion of rGO multiplayers. Figure 3c shows the overall cross-section image of Au-rGO lithiated at 2 mA h cm\(^{-2}\). Figure S4 in the Supporting Information shows the top-view SEM image of Au-rGO electrodes after depositing 2 mA h cm\(^{-2}\) of lithium. It can be seen that the surface is smooth. No lithium dendrites are observed on the top of the electrode. The thickness of Au-rGO electrode increases from 12 to about 16 µm with lithium plating.

It is also noted that the Au-rGO samples maintain the generally flat morphology during cycling. Especially, the parallel edges of rGO sheets in the expanded anode are the evidence that lithium is uniformly plated between layers because a nonuniform plating may not lead to parallel layer morphologies. After fully stripping lithium, the layered morphology of rGO sheets is restored (Figure 3d). In contrast, lithium plating on a planar Cu foil produces a significant amount of dendrites as shown in Figure 3e. Without uniformly dispersed Au NPs inside, rGO exhibits the lithium plating on the top surface. The nonuniform lithium deposition can be distinguished by the morphology difference on the top and bottom layers in Figure 3f. The optical photo in the inset of Figure 3f shows lithium spots on the overall black rGO film. As compared to Li-plated Au-rGO, these lithium spots further confirm nonuniform deposition on the electrode level. Nonuniform plating on either microscales (like on Cu foil) or electrode levels (like on rGO) should be avoided because the nonideal lithium deposition ultimately leads to serious safe issues.

The results of lithium plating/stripping in Figure 3 reveal that Au NPs could induce relatively uniform lithium plating inside the electrode structure. However, how lithium atoms distribute in the 3D electrode structure still needs to be further clarified. To determine this, the Li-plated samples were cleaned with the fresh solvent (dimethyl carbonate). Because lithium atoms cannot be effectively detected with a conventional energy-dispersive X-ray (EDX) mapping technology, we allowed oxygen to diffuse into the dried samples and slowly react with lithium. Figure 3g–i shows the SEM and elemental mapping images of Au-rGO and j–l) rGO which were plated with lithium and oxidized in dry air.
the strong oxygen signals in Figure 3I. EDX mapping results confirm the uniform distribution of lithium inside the whole Au-rGO electrode.

Metallic lithium–based anodes usually suffer from low CEs, which limit their practical applications. To determine whether Au NPs pillared rGO films could improve the CEs of lithium anodes, rGO, Au-rGO, and Cu foil anodes were assembled with lithium and cycled with a limited capacity of 2 and 5 mA h cm$^{-2}$, respectively. Figure 4a shows that all three samples have low initial CEs, which gradually rise above 94.5% in about ten cycles. The Cu foil electrode decays rapidly since the 50th cycle. The CEs of the rGO cell are generally lower than those of Au-rGO but higher than those of Cu foil. Starting with the 60th cycle, rGO shows a significant CE decay. When the capacity (Figure 4b) or the current density (Figure S5, Supporting Information) is increased, Au-rGO could still exhibit the highest CEs. The CEs of the Cu foil cell decrease most rapidly, especially at the high capacity charge of 5 mA h cm$^{-2}$. As shown in Figure 4b, the rGO sample loses about 22.9% of CE from the 44th to 52th cycles. The CEs changes are influenced by the continued consumption of cyclable Li-ions for the SEI formation, which is highly correlated to the lithium deposit morphologies as shown in Figure 3. The dendrite formation on Cu foil indicates relatively large lithium/electrolyte contact, which induced a high amount of SEI. When dendrites are stripped, the morphology changes further aggravate the SEI issues and even leave dead lithium electrically isolated.[40–43] For the rGO sample, lithium plating mainly occurs on the top surface of rGO. The adhesion of lithium to rGO in Figure 3f may imply that lithium was unevenly filled into the top few multilayers. Such a morphology of plated lithium reduces the surface area and improves the CEs as compared to Cu foil.

As we demonstrate here, the Au NPs induced lithium plating between rGO sheets and improve the CEs, probably because the lithium/electrolyte contact area was reduced and replaced with rGO/lithium/rGO contact. The volume change during lithium plating/stripping was restrained to the through-plane direction. Figure S6 in the Supporting Information shows the thickness change with the plating/stripping capacities. When lithium was plated with capacities of 2.5 and 4 mA h cm$^{-2}$, the thickness of Au-rGO electrode (12 µm) increased to ≈18.5 and ≈25.6 µm,

![Figure 4](image-url)

Figure 4. Coulombic efficiencies of Au-rGO, rGO, and Cu foil at 0.5 mA cm$^{-2}$ with the capacity limited to a) 2 and b) 5 mA h cm$^{-2}$. c) Voltage profiles of lithium plating/stripping. The inset is nucleation section on the voltage profiles. Comparison of electrochemical properties of three symmetric cells consisting of three samples: d) voltage–time profiles of lithium plating/stripping cycles with a limited capacity of 2 mA h cm$^{-2}$ at 0.5 mA cm$^{-2}$; e) voltage hysteresis variation with cycling number; f) detailed voltage profiles of the 1st, 40th, 70th, and 100th cycles; g), h) Nyquist plots of Cu foil, rGO, and Au-rGO cells in the 5th and 80th cycles.
respectively. After lithium was stripped, the thickness returned to \( \approx 12 \, \mu m \). The in-plane morphology changes may be minimized because the uniformly distributed Au NPs provide the equal nucleation probability and even similar out-of-plane growth rates. This could be derived from the overall parallel alignment of rGO sheets at fully plated and stripped states (Figure 3c,d). As illustrated in Figure 1e, the main SEI formation may occur on the top surface and remain minor changes during cycling. Such an interlayer lithium plating process in Au-rGO may be the main reason for the high CEs. Figure S7 in the Supporting Information shows that during lithium plating/stripping, the Au-rGO electrode is able to maintain the thickness at \( \approx 16 \) and \( \approx 12 \, \mu m \), respectively, indicating that the Au-rGO structure has good stability upon cycling.

Figure S8 in the Supporting Information presents the rate properties of the Au-rGO electrodes. The overpotentials increase with the current density. The deliverable capacity decreases, yielding low CEs. Figure 4c shows the voltage profiles of lithium plating/stripping in the Au-rGO, rGO, and Cu foil samples. Cu foil presents the steep voltage drop and nearly zero capacity above 0 V (vs Li/Li\(^+\)), which are in agreement with the fact that lithium does not alloy with Cu. For the Au-rGO sample, the sloping voltage profile above 0 V (stripping curve) is mainly caused by lithium alloying (dealloying) with Au. Most of the capacity of Au-rGO is delivered below 0 V by lithium plating. The slope value of the rGO lithiation/delithiation curves above 0 V resides between Au-rGO and Cu. The capacity of rGO in the sloping region may be contributed by the unreduced functional groups which react with lithium at positive voltages.\(^{[43–47]}\) The voltage dips on the plating curves are caused by the nucleation energy barriers (Figure S1a, Supporting Information). The voltage dips on the lithiation voltage curve because Au-Li alloys have interactional groups which react with lithium at positive voltages.\(^{[44–47]}\) The semicircle diameter is proportional to the total resistance of Li-ion migration through these multilayers. Figure 4g,h shows that the semicircle diameters of the Cu foil and rGO samples increase from 12.4 and 13.0 \( \Omega \) in the 5th cycle to 37.3 and 19.1 \( \Omega \) in the 80th cycle, respectively. It indicates the thickening film of SEI. In contrast, Au-rGO builds up less SEI than Cu foil and rGO because its semicircle diameter remains almost unchanged. In conjunction with the SEM observation, it seems to imply that Au-rGO forms low-resistance SEI film and maintains the SEI structure well during repeated lithium plating/stripping, yielding the low-voltage hysteresis and high CEs. The Cu foil and rGO cells continuously consume lithium ion and build up SEI films, leading to the high-resistance film and low CEs. Eventually, the dendrites proceed into separator and cause the cell breakdown. Thus, Au NPs pillared rGO demonstrates the high cyclability as compared to Cu foil and rGO cells.

Figure S5a shows the postmortem SEM images of Au-rGO and rGO. The Au-rGO electrode remains the compact structure after 20 cycles. The smooth surface and complete monolithic structure indicates the good cyclability. Figure 5b shows that dendrites were formed on the top surface of Cu, rGO, and Au-rGO, it can be concluded that adjusting lithium nucleation in 3D electrodes using Au NPs is able to induce lithium growth to occur at the locations which usually exhibit high mass transport resistances. Because the nonuniform resistance distribution readily leads to the selective nucleation where the minimum resistance exists, our Au-rGO structure is designed to minimize the nonuniform plating by embedding easily nucleating Au NPs in the high resistance regions. The long-term cycling properties were tested in symmetric cells consisting of two identical electrodes. The cycling capacity was limited to 2 mA h cm\(^{-2}\). Figure 4d shows that about 0.022–0.028 V overpotentials are needed to drive a current density of 0.5 mA cm\(^{-2}\) in the first few cycles for all three samples. The overpotential of the Cu foil cell increases from \( \approx 0.023 \) to \( \approx 0.1 \) V after 100 cycles. It abruptly drops to \( \approx 0.078 \) V in the 120th cycle. The rGO cell shows the relatively slow increase of overpotentials until 80 cycles. There is a rapid increase of overpotentials between the 80th and 100th cycles. Since the 100th cycle, the overpotential per cycle starts to oscillate, implying the unstable Li/electrolyte interface. In contrast, the Au-rGO cell demonstrates the highest overpotential stability up to 200 cycles for 1600 h. It is not until the 195th cycle that the overpotential of Au-rGO starts to rise.

Figure 4f shows the voltage profiles of several typical cycles. In the first cycle of Figure 4f, there is a dip for Cu foil and the overpotential of Au-rGO is slightly more negative than those of Cu and rGO. These results resemble the initial voltage profile as the half cells show in Figure 4c. The Cu foil cell shows the noisy voltage profile in the 70th and 100th cycles of Figure 4f, indicating the unstable SEI film. The abrupt voltage drops of the Cu foil cell in Figure 4a,e imply the microshort caused by dendrites growth. With cycling, the lithium plating overpotentials for Au-rGO remain almost constant. Cu and rGO require more driving forces to maintain the current density of 0.5 mA cm\(^{-2}\). The voltage hysteresis for each cycle in Figure 4e further quantifies the increase of driving forces, implying the SEI build-up. The Nyquist plots of three samples show the depressed semicircles, which could be explained by "Voigt"-type equivalent analogs of resistor-capacitor (RC) circuits in series.\(^{[43,48]}\) Each RC circuit represents an interface for lithium transfer. The SEI film may consist of multiple layers of such interfaces.\(^{[43]}\) The semicircle diameter is proportional to the total resistance of Li-ion migration through these multilayers.
growth are sandwiched between rGO sheets, leading to the stable SEI formation and electrode structures.

3. Conclusion

Au NPs pillared rGO film was fabricated to induce lithium nucleation and growth between rGO sheets. Lithium plating/stripping in the Au-rGO sample is superficially similar to the intercalation reactions in the layered structure. The through-plane thickness decreases and increases with lithium stripping and plating, respectively. However, the main framework of rGO sheets retains the parallel stacking morphology. Such an interlayer lithium plating mode differs significantly from the surface plating mode, which usually occurs on Cu foil and rGO samples. The mechanism which drives for lithium deposition between the rGO layers is the low nucleation energy barrier provided by the gold in the Au-rGO electrode counterbalances the preference of lithium to plate in regions with the highest Li-ion concentration, which is manifested by intrinsic nonuniformity of unavoidable mass transport resistance in real electrodes. The interlay lithium plating relatively suppresses surface deposition. The rGO/electrolyte contact replaces most of lithium/electrolyte interfaces, yielding a stable SEI, which is protected by the stable electrode structure and morphology. As a result, Au-rGO demonstrates a high CE of 98% for at least 200 cycles with a high capacity of 2 mA h cm\(^{-2}\) for 1600 h.

4. Experimental Section

Fabrication of Au NPs Pillared rGO Film: GO was prepared according to Hummer’s method.\(^{(49)}\) About 50 mg GO powder was first dispersed in 50 mL deionized water by ultrasonication and stirring. When the mixture was well dispersed, about 10 mg HAuCl\(_4\) and 0.1 g sodium citrate were added into the GO suspension. The suspension was stirred for 0.5 h and then heated at 80 °C for 2–3 h. After being washed and centrifuged three times, the suspension was vacuum filtrated to fabricate a monolithic film. The resulting film was further reduced within hydrazine hydrate steam at \(\approx 200 °C\) to obtain Au-rGO film.

Materials and Electrochemical Characterization: The XRD patterns were measured by a Rigaku D/Max III X-ray diffractometer with Cu K\(_\alpha\) radiation (\(\lambda = 1.5418 \text{ \AA}\)). The SEM images and EDX mapping were obtained using a field-emission scanning electron microscope (Zeiss Ultra 55). The high-resolution TEM (HRTEM) images were recorded on a FEI Tecnai F20 microscope at 200 kV. All the coin cells were assembled in an Ar-filled glove box. Celgard 2700 membrane was used as the separator. The electrolyte was 1 M lithium bis(trifluoromethane)sulfonimide (LiTFSI) in a 1:1 volume ratio mixture of 1,3-dioxolane and 1,2-dimethoxyethane with 1% LiNO\(_3\). About 50 \(\mu\)L electrolyte was dropped into each cell. The assembled cells were precycled between 0.01 and 1 V at 200 \(\mu\)A cm\(^{-2}\) for five times to stabilize the SEI formation according to previous reports.\(^{(50–52)}\) After that, the galvanostatic charge/discharge protocols were applied to characterize the electrochemical properties of the precycled cells on a Land Battery Tester (Wuhan LAND electronics Corp. China). Electrochemical impedance spectroscopy (EIS) measurements were conducted between 100 KHz and 100 mHz within a VSP potentiostat (Bio-Logic Corp.).

Supporting Information

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

Acknowledgements

This work was supported by the National Science Foundation of China (21776121), the National Key Research and Development Program of China (No. 2017YFA0205700), the Thousand Youth Talents Plan, the Jiangsu Outstanding Youth Funds (BK20160012), the National Materials Genome Project (2016YFB0700600), the “Jiangsu Shuangchuang” Program, and the Nantong Fundamental Research Funds (GY12016040).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

gold nanoparticles, intercalation, interlayer plating, lithium anodes, reduced graphene oxides

Received: June 15, 2018  
Revised: July 13, 2018  
Published online:

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