Graphene-Coated Aluminum Thin Film Anodes for Lithium-Ion Batteries

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ABSTRACT: We present a detailed study on graphene-coated aluminum thin films for Li-ion battery anode applications. The best electrode ageing behavior is obtained for Al films encapsulated with four porous graphene layers. Graphene encapsulation prevents “crushed” Al nanoparticles from detaching from the anode, thus allowing prolonged charge-discharge cycling. Graphene also provides surface conduction paths for electrons as well as diffusion paths for Li atoms. For the first time, we report the electrochemical room temperature formation of phases such as Li1Al2 and even Li2Al3 with a higher Li content than β-LiAl. More interestingly, we observe a progressive change of the composite thin film electrode, switching from a pure galvanic to a pseudocapacitive behavior as the size of the Al grains decreases from ~100 to 5–10 nm due to repeated Li alloying-dealloying. The capacity values of ~900 and 780 mAh/g are obtained after, respectively, 500 and 1000 charge-discharge cycles at 0.1C. Our results may refocus the interest of the battery community on Al-based thin film anodes, since they are potentially very simple to fabricate, particularly if porous graphene is replaced in the future by reduced graphite oxide.

KEYWORDS: Li-ion batteries, aluminum anodes, nanoporous graphene, lithium-aluminum compounds, prolonged cycling

INTRODUCTION AND CONTEXT

Although rechargeable (secondary) Li-ion batteries (LIBs) are standard and established commercial products generating billions of dollars of turnover every year, they still suffer from a number of drawbacks, such as limited capacity, long charging/discharging times, and a relatively short lifetime of ~200 to ~1000 cycles depending on the way they are used.1 In a standard commercial LIB, Li ions are shuttled back and forth between a graphite anode and a layered oxide cathode as the battery is charged and discharged.2 Graphite is the most reliable anode material, since it can host lithium atoms by a topochemical intercalation reaction, leading to only ~10% increase of the interlayer graphite spacing and less than 1% expansion in the basal graphite plane.3 However, at maximum intercalation, the capacity of a pure graphite electrode is only 372 mAh/g, corresponding to the LiC6 compound.

To meet the requirements of next generation electric vehicles, lithium-based batteries have to be improved not only in terms of capacity, but also in terms of the cycling rate and lifetime. As far as anodes are concerned, alloying Li with various metals or semiconductors (Sn, Sb, Al, Si, etc.) represents an alternative to the use of graphite, in particular, concerning the increase of capacity.4,5 Although the major contenders are tin5,6 or silicon,7 aluminum is also an interesting anode material since it can form a series of solid solutions and intermetallic compounds with Li,8 culminating at a theoretical capacity of 2235 mAh/g for the Li9Al4 compound of the equilibrium phase diagram. Moreover, Al is the third most abundant element on earth, and it is environmentally friendly and relatively cheap. Al can be easily deposited by various techniques, such as vacuum thermal evaporation or sputtering,9 chemical vapor deposition (CVD) from organometallic compounds (see e.g., ref 10), or electrodeposition in electrolytes based on ionic liquids.11 Finally, since Al is a metal, contacting it with the anode current collector (usually a Cu foil) poses no interface problem, in contrast with Si which is a semiconductor and may induce a Schottky barrier at the contact.
Early studies concerning the electrochemical room temperature (RT) alloying of Li with an Al electrode were performed more than 40 years ago, and it was rapidly believed that Al or Li−Al alloys could replace pure lithium in secondary Li-ion battery anodes, thus circumventing the problem of Li dendritic growth upon battery charging. Unfortunately, prelithiated Al electrodes were found to disintegrate after a few charge−discharge cycles, because of large volume variation and phase change upon Li deinsertion/insertion. The use of Al thin films, micro- and nano-sized Al particles, or composites did not improve the cycling behavior significantly. On the basis of the mixed-conductor matrix concept, binary or ternary Al-based alloys were also investigated. However, in most studies, the number of charge−discharge cycles was limited to, at best a few tens, which is not enough to decide on the viability of an Al-based electrode. One of the best results (i.e., 50% retention of the original capacity after 100 charge−discharge cycles) was obtained by using Al0.5Cu0.5 binary alloys synthesized by vacuum sputtering. Also, the RT electrochemical alloying of Li with Al seems to be limited to the β-LiAl intermetallic compound of the Al−Li phase diagram, corresponding to a capacity of 993 mAh/g. β-LiAl crystallizes in the so-called Zintl structure (space group Fd3m), which can be described as two interpenetrating diamond lattices with each element occupying one of the lattices. The lattice parameter of β-LiAl at stoichiometry is ~6.3 Å and its elemental cell accommodates eight Al atoms, so that transforming Al (face-centered cubic structure, with a lattice parameter of 4.05 Å) into β-LiAl yields a ~95% volume expansion per Al atom. Clearly, the Al to β-LiAl transition upon electrochemical alloying with Li involves strong restructuring of the Al lattice.

Recently, one-dimensional Al nanostructures, such as nanowires, nanorods, or nanorods have been tested as battery anodes, but here again, the original capacity quickly fades away after a few cycles, even quicker than with thin films. This behavior is in stark contrast with that of other elements or alloys (particularly Si), where the use of such one-dimensional nanostructures is found to improve the cycling behavior (see e.g., refs 31−35). We note, however, that good characteristics (1200 mAh/g after 500 cycles) have recently been obtained for an Al-based anode using yolk−shell nanostructures with an Al core (30 nm in diameter) surrounded by a TiO2 shell of about 3 nm thick. In another recent report, the authors have built Al−C nanoclustered anodes from C60 and Al precursors deposited by combining thermal evaporation and plasma-enhanced chemical vapor deposition; they have also obtained good cycling characteristics.

Several reasons have been invoked to explain the rapid failure of Al-based anodes. For instance, Hudak and Huber have noted that after 25 charge−discharge cycles, Al thin films were transformed into a highly porous three-dimensional structure. They rule out the loss of particles from the anode as a reason for capacity fading; rather, they suggest that within the continuous electrode structure, there exist some voids or non-conductive phase, which decrease the ionic or the electronic conductivities. They also note that during lithiation, the native surface oxide (Al2O3) is transformed into a glassy Li−Al−O material which is an electronic insulator and does not revert to Al upon delithiation, thus irreversibly trapping some Li. Consequently, the larger the surface area (e.g., in nanostructures), the stronger the Li trapping effect; this would explain why the capacity of nanowires and nanorods fades away more rapidly than that of thin films. In another recent report on thin-film-type batteries, the authors advocate Li and Al trapping in β-LiAl due to the lack of surface pathways allowing Li and Al to out-diffuse from the β-LiAl domains upon delithiation. In ref 36, the authors point towards the mechanical instability of the solid-electrolyte interphase (SEI) layer due to the large volume change experienced by the Al-based electrode during lithiation/ delithiation, a problem otherwise well identified for Si-based anodes.

In the present work, we have used a composite Al-based anode structure, where layers of nanoporous graphene (NPG) are laid on top of the surface of Al thin films. The NPG layers provide a surface conducting path which prevents Al particles from being electrically isolated from the current collector, even if voids or nonconducting phases are created underneath them, within the bulk of the film; the NPG layers also provide surface diffusion paths for Li to out-diffuse from β-LiAl or any other Li−Al compound that would have formed during electrochemical alloying. Finally, NPG stabilizes the SEI by avoiding direct contact between Al and the electrolyte. When the Al thin film is covered with four layers of NPG, we obtain a capacity of ~900 mAh/g after 500 charge−discharge cycles at 0.1C. More importantly, we observe that the anode progressively evolves from a pure galvanic behavior to a pseudocapacitive behavior after a few hundred cycles; in particular, no Li−Al phase (whether β-LiAl or Li3Al2 or Li9Al4) appears anymore at the end of the lithiation step. We correlate this intriguing behavior to a progressive decrease of the Al grain size, which is accompanied by a concomitant increase of the surface of grain boundaries (and surface/interface energy), as the number of charge−discharge cycles increases. We believe that this increase in the surface/interface energy, associated with the strain generated by a phase change leads to the build-up of a nucleation barrier which is just too high to be overcome by any of the lithiated phases likely to appear upon alloying.

At this point, we emphasize that graphene encapsulation has already been used as an anticorrosion coating for the current collector (Al foil) of Li-ion battery cathodes, which is a totally different application, where graphene’s porosity is of course proscribed. Mixtures of graphene and carbon nanotubes have also been tested to improve the sulfur contact to the Al current collector in sulfur-based cathodes. In another study, reduced graphite oxide (r-GO) has been employed for encapsulating Li metal anodes, thus mitigating the long-standing problem of dendritic growth; r-GO has been utilized as a spongy scaffold to host Li metal, also alleviating the dendrite growth problem.

### RESULTS AND DISCUSSION

Since graphene is impervious even to helium, the graphene lattice has to be rendered nanoporous so that Li ions can travel through it to reach the Al thin film. Therefore, we devoted our first efforts to the reproducible fabrication of NPG membranes. For the experiments described in this work, we have used CVD-grown graphene on electropolished Cu foils (see Methods and refs 44, 45) as the precursor for NPG. Actually, CVD-grown graphene allows us to accurately control the number of layers transferred on top of the Al thin films, a control otherwise difficult with graphene synthesized by a simpler chemical approach (e.g., by the reduction of graphite oxide, see ref 46). Figures S1 and S2 (Supporting Information) show the preparation of the Al-based anodes, with NPG sheets.
on top. Al was first evaporated to thicknesses of 300−800 nm (corresponding to 80−220 μg/cm²) on Cu foils acting as anode current collectors. During the course of our experiments, we have observed that asperities or protrusions on the Al surface were inducing cracks and rips in the NPG membranes. We strongly suspect that these surface defects locally pin the NPG membranes, thus, preventing them from sliding with respect to each other when the Al volume increases, due to swelling upon Li uptake. Therefore, to obtain a smooth Al surface, free from protruding defects, we have decided to use electropolished Cu foils as anode current collectors, underneath the Al thin films. In other words, the preparation of the anode Cu current collector, before Al deposition, is similar to the preparation of the Cu foils before graphene growth,44,45 except that no high temperature annealing is performed for the anode Cu current collector. To improve adhesion, the Al films are baked at 250 °C for 1 h after evaporation on Cu. Concerning the final anode structure, we have varied the number of NPG layers transferred over the Al thin film between 1 and 8.

Each NPG sheet was prepared according to the method described by Lee and co-workers,47 whereby the graphene samples were placed face down in a plasma generator (see Methods), to avoid direct ion bombardment. After CVD growth, the graphene samples (still sitting on their Cu substrates) were directly loaded in the plasma reactor. The O₂ pressure and flow were kept constant (0.1 bar, 30 sccm), whereas the power (from 6 to 20 W) as well as the etching time were varied (from 0.5 to 5 s). Figure 1 shows some characterization of graphene sheets after treatment in the oxygen plasma under various conditions. For Raman analysis (see Methods), the etched graphene sheets were first transferred onto oxidized Si substrates (Si/SiO₂) using the standard poly(methyl methacrylate) (PMMA)-based process (see Methods and ref 48).

As shown in Figure 1a, for very soft etching conditions (6 W, 0.5−5 s), the Raman spectra present the general signature of a high quality graphene single-layer (0 s), with a G peak at ~1593 cm⁻¹, a 2D peak at ~2680 cm⁻¹, an I₂D/I_G ratio of 3.8, and no D peak at ~1343 cm⁻¹, the latter corresponding to defects in graphene (see e.g., ref 49 for the assignment of the various Raman peaks of graphene). From 10 W and 1 s etching conditions, a tiny D peak starts to appear, indicating the formation of defects. For longer or stronger etching conditions, the D peak intensity sharply increases, a D’ peak appears,50 while the 2D and G peaks, as well as their relative intensities decrease. These are clear indications of the presence of large defect quantities in the graphene layers. Since we want to transfer graphene onto Al after oxygen etching, we preferably need slightly damaged and continuous porous sheets. Consequently, the etching conditions corresponding to the onset of apparition of defects (10 W, 1 s) might be appropriate. This is confirmed by observing the morphology of a NPG sheet (etched with 10 W for 1 s) under a transmission electron microscope (TEM), Figure 1b; randomly distributed pores can be observed, with their sizes below...
10 nm. We believe that the black contrast areas in the TEM picture of Figure 1b are due to both (i) local folding of the graphene sheet and (ii) PMMA residues from the graphene transfer step. Actually, since we were interested in the pore size, as well as pore distribution and since the graphene was not intended for electrical measurements, we did not thoroughly clean it after transfer. The electron diffraction pattern recorded on the same sample (Figure 1c) shows the typical features of single-layer crystalline graphene; this confirms that the overall crystalline structure of graphene is preserved during O₂ etching. These optimized conditions (O₂ plasma, 0.1 bar, 30 sccm, 10 W, 1 s) were confirmed over five samples (by Raman and TEM), before being routinely used to fabricate NPG membranes for all the Al-based anodes presented in the following part of this paper. After oxygen plasma etching, the Cu foil was etched away and each NPG membrane was transferred on top of the Al thin film by the standard PMMA-based process (Methods) and various electrochemical tests were performed.

As shown schematically in Figure S1, the NPG-Al on Cu anodes was mounted in Swagelok-type cells for further battery testing in a half-cell configuration, against a pure Li foil (see Methods). Each anode was characterized in galvanostatic conditions as well as by cyclic voltammetry.

The first galvanostatic anode testing in a half-cell configuration with only one NPG sheet resulted in limited success, compared to the bare Al film on Cu (see Figure S3, Supporting Information). Consequently, we performed a series of preliminary galvanostatic tests to evaluate the effect of the NPG number on the cycling characteristics of NPG-Al on Cu anodes. Figure S3 (Supporting Information) compares the aging behavior of the bare Al on Cu anode with that of samples covered with various numbers of NPG sheets; in the following, NPGn means that n layers of NPG have been sequentially transferred and stacked on top of the Al thin film. Inspection of Figure S3 shows that NPG4-Al on Cu exhibits the best behavior in terms of resistance to cycling (see the curves summarizing this in Figure S3, panel f). We believe that when n is small (1 ≤ n < 3), cracks easily develop in the NPG membranes as the Al volume increases upon lithiation; this leaves large parts of the Al membrane directly exposed to the electrolyte, so that the anode behavior resembles that of the uncoated Al and the capacity fades away rapidly. On the other hand, when the number of NPG layers is high (say n ≥ 6–7), Li ions cannot easily diffuse through the stack of NPG layers (as already evidenced in ref S1) and we observe the formation of a thick SEI layer, that probably blocks Li diffusion/permeation. Having decided that n = 4 is a good compromise, we then proceeded to study carefully NPG4-Al on Cu (NPG4-Al/Cu) anodes.

Figure 2 shows detailed galvanostatic (potential window from 0 to 3 V; 0.1C rate) and cyclic voltammetry (between 2 and 0 V, at a scanning rate of 0.05 mV/s) characterizations of the NPG4-Al/Cu anodes during the first few charge–discharge cycles. Voltages are measured versus Li⁺/Li₀. Upon lithiation, when the voltage goes below 250 mV, these second sloping plateaus indicate a second (very rapid) equilibrium, between β-LiAl and another Li–Al alloy of a higher Li content (see Figure S4).

X-ray diffraction analysis experiments performed at the end of the first lithiation step clearly identify the rhombohedral (R3m) Li₄Al₂ compound (see Figure S4c). Note that after the SEI has formed and the electrode has stabilized (say after the first two cycles) the lithiation/delithiation capacity of ∼1250 mAh/g (see the galvanostatic curves for the third and fifth cycles on Figure 2a) is close to the theoretical capacity of the Li₄Al₂ compound (1486 mAh/g).

The cyclic voltammetry curves of Figure 2b show two peaks upon lithiation, which correspond to reactions between Al and β-LiAl (∼100 mV) and β-LiAl and Li₄Al₂ (close to 0 mV). Compared with uncapped Al, the NPG4-Al/Cu anode shows a sharper peak during the first lithiation (Figure S5, note the hump on the right-hand side of the first peak for the uncapped
Al anode), indicating that NPG mitigates electrolyte decomposition and SEI formation.

Upon delithiation, the galvanostatic curves first show a steep rise, up to ~100 mV. Then, from 100 mV, the slope changes, until a plateau appears around 500 mV. The plateau at ~500 mV corresponds to the continuous extraction of Li from β-LiAl, leading to the formation of Al (equilibrium between β-LiAl and Al). Things are less clear between 100 and 500 mV. We believe that the change of the slope around 100 mV marks the onset of decomposition of Li3Al2 into β-LiAl, but also into Al, as indicated by the X-ray diffraction spectrum of Figure S6a (taken when delithiation is stopped at 250 mV) where the three species are clearly identified. We repeated this experiment several times and always found these three species. The decomposition of Li3Al2 is very fast and it probably occurs totally out of thermodynamic equilibrium. X-ray diffraction analysis performed when delithiation is stopped at 300 mV indicates that Li3Al2 has already totally disappeared as only Al and β-LiAl are identified (Figure S6b); however, this result is rather puzzling since the equilibrium between Al and β-LiAl should correspond to a voltage of 500 mV (instead of 300 mV). We suspect that once triggered, the decomposition of Li3Al2 keeps going, even when the delithiation voltage is turned off, so that by the time the samples are brought to the X-ray diffraction instrument, Li3Al2 has disappeared. We observe the same effect when delithiation is stopped at 480 mV, i.e., before the plateau corresponding to the equilibrium between β-LiAl and Al (see Figure S6c).

Still, upon delithiation, the cyclic voltammetry curves (Figure 2b) show a broad peak starting at ~500 mV and ending up at 750 mV. However, this broad peak is not symmetric and upon close inspection, a hump can be observed on its left-hand side, which indicates that it is composed of at least two subpeaks, the first one corresponding to the decomposition of Al2Li3, followed by a second one corresponding to the decomposition of β-LiAl.

Figure 3 shows the ageing behavior of the NPG4-Al/Cu anode tested at a charge–discharge current of 140 mA/g (0.1C). (b) Cycling the anode with an increasing C rate. The straight line corresponding to 1000 mAh/g is just a guide for the eye.

Figure 4. Various X-ray diffraction analysis performed at the end of lithiation steps. (a) Reference before lithiation, (b) after first lithiation, (c) after 10th lithiation, (d) after 35th lithiation, (e) after 250th lithiation.

capacity value of 2235 mAh/g for the Li9Al4 compound and the measured value (~1600 mAh/g), as if only a fraction of the starting Al material was taking part in the electrochemical transformations. The surface Al native oxide (Al2O3), together with the oxygen segregated at grain boundaries probably account for some of this difference, having in mind that AlO2 is irreversibly transformed into a (Li-conducting) Li–O–Al glass during the first lithiation,29 thus trapping some of the starting Al material (as well as some of the Li, as already quoted above). Also, it is not clear why the Li9Al4 compound appears only after a few tens of charge–discharge cycles; maybe the formation of other phases (with a lower Li content) is prevented by strain effects (see below). This observation calls for more detailed studies of Li alloying with graphene-coated
Al in the future. Maybe the most interesting result of these X-ray investigations is that for the 250th cycle, we only find Al at the end of the lithiation step. The corresponding galvanostatic and cyclic voltammetry curves (250 cycles) displayed in Figure 5 confirm that there are no phase equilibria anymore, as the characteristic alloying/dealloying features (plateaus and peaks) have disappeared from the lithiation and delithiation curves. There are examples in the literature showing similar changes in galvanostatic characteristics as the grain size of the Li storage material decreases in the few nanometer range.

Actually, our transmission electron microscopy (TEM) analysis of the Al structure after delithiation indicates a clear decrease in the grain size as the number of cycles increases (see Figure 6). Indeed, while the grain size of Al after deposition is around 100 nm (Figure 6a), it falls down to 5–10 nm after 250 charge–discharge cycles (Figure 6d). This decrease in the grain size can be understood from the experiments of ref 29, where the formation of voids was clearly observed in monocrystalline Al nanowires already after the first delithiation. These voids result from the removal of Li from the β-LiAl alloy and their size and number increases with the number of cycles. Hence, we can here imagine the same kind of mechanism, which would divide the Al grains further and further as a consequence of repeated dealloying, leading in the end to very small sizes. In our situation, the asymptotic size limit of the Al grains seems to be between 5 and 10 nm, corresponding to a situation where alloying during lithiation does not take place anymore (see Figure 4e, as well as Figure 5). This observation raises two main questions: why alloying does not take place anymore below a certain Al grain size? And where is the Li stored if it does not form an alloy with Al?

First, it has been shown that the nucleation of β-LiAl inside an Al matrix is difficult, due to the large strain associated with the change in the corresponding molar volume. This is evidenced here by a small voltage drop below 250 mV in the galvanostatic lithiation curves as shown in Figure 2, which we have attributed to a large nucleation barrier (see above the comments of Figure 2). As the Al grain size decreases, the total Al surface (i.e., the total surface of grain boundaries) increases and so does the overall surface/interface energy. So, assuming that each Al grain transforms into β-LiAl, there is a point where the energy cost in overcoming the surface energy + strain energy becomes too high, thus preventing the nucleation of the β-LiAl phase; in other words, the barrier for the nucleation of a lithiated phase becomes just too high when the Al grain size is in the 5–10 nm range.

Concerning the location of Li, it can be either at the surface of Al grains (i.e., at grain boundaries) or as a solid solution in Al (or at both locations). Several papers have highlighted changes in phase diagrams (both movement of phase boundaries to lower temperatures and increase in solubility for α-type phases) as the particle size decreases. Hence, assuming an increase of the Li solubility in Al (say up to 5%, which is probably exaggerated) due to the nanometric size of the Al grains, we obtain a ~50 mAh/g capacity value, which cannot account for what we measure after 250 cycles (~1000 mAh/g). Now, assuming an Al grain size of 5 nm as well as cubic Al particles, we calculate a total surface of grain boundaries of ~180 cm² per cm² of foot print of the anode, for a 300 nm thick Al thin film. Note that this surface area is probably an underestimation, since we have implicitly assumed atomic flatness of the surface of the cubic Al grains, which is not the case (see TEM pictures, Figure 6). If we take 1.15 × 10¹⁵ atoms/cm² as the monolayer Li density (corresponding to the density in a (110) crystallographic plane of body-centered cubic Li), then we obtain ~2 × 10¹⁷ Li atoms/cm² of foot print, which corresponds to a charge of 3.2 × 10⁻² C (i.e., ~9 × 10⁻₃ mAh/cm² of the foot print of the 300 nm thick Al anode. Dividing this value by the mass of the 300 nm thick Al film per cm², we finally obtain a capacity of 110 mAh/g for each monolayer of Li adsorbed on the surface of the Al grains. Hence, to account for the observed capacity, we would need 8–9 layers of Li adsorbed on the surface of grain boundaries, probably even less since the grain boundary surface area was underestimated, as explained above.

Another question that may arise now is why we do not see any metallic Li in the X-ray spectrum of Figure 4e? It is well-known that Li, due to its low electron density, lightly interacts with X-rays, particularly in the presence of elements exhibiting much higher electron densities (such as Al). Moreover, the Li thickness is expected to be very small (<10 monolayers) and Li is probably ill-crystallized, which are other reasons for the absence of X-ray response.

In conclusion, we have presented in this work a novel way of using Al thin films as anodes for Li-ion batteries. Encapsulating the Al films with graphene sheets prevents Al particles from detaching from the anode during prolonged charge–discharge cycling. This is summarized in Figure 7, where we have shown schematically that graphene layers can slide with respect to each other when the electrode volume increases/decreases, thus still providing the desired conducting/diffusing/encapsulating effects, which prevent rapid electrode disintegration. For
the first time, phases beyond $\beta$-LiAl have been identified in a thin film of Al upon room temperature electrochemical lithiation. Due to the formation of these phases with a high Li content ($\text{Li}_3\text{Al}_2$ and $\text{Li}_9\text{Al}_4$), the electrode capacity peaks at $\sim 1600 \text{ mAh/g}$. The capacity values of $\sim 900$ and $780 \text{ mAh/g}$ are found after, respectively, 500 and 1000 charge−discharge cycles at a 0.1C rate. More importantly, the electrode is found to evolve from a purely galvanic to a pseudocapacitive behavior (i.e., no phase change, but change in the oxidation number of Li), as the grain size of the active Al material decreases from $\sim 100$ to 5$-$10 nm due to repeated charge-discharge cycling.

**Figure 6.** Transmission electron microscopy (TEM) analysis of the grain size evolution of Al as the number of charge−discharge cycles increases. (a) After Al deposition, (b) after 10 cycles, (c) after 25 cycles, and (d) after 250 cycles; note the extremely small grain size (below 10 nm). The TEM observations in (b), (c), and (d) have been performed after complete delithiation.

**Figure 7.** Schematics summarizing the fabrication of the graphene-coated Al anode, as well as a lithiation−delithiation cycle of this anode. (a) Oxygen plasma etching of a CVD-grown graphene sheet, yielding nanoporous graphene (NPG). (b) Transfer of four NPG layers on the Al thin film. (c) The lithiation step where the graphene layers slide independently to accommodate the volume expansion of the anode and maintain the electrical contact between the Al surface and the Cu current collector. (d) Delithiation and “crushing” of the Al thin film. (e) Delithiated Al thin film; note the change in the grain size for the Al thin film.
transferred CVD graphene could easily be replaced in the future by much cheaper and commercially available reduced graphite oxide (r-GO). The promising results presented here call for more studies into the Li interaction mechanism with graphene-encapsulated Al thin films, to better understand the alloying–dealloying mechanisms and further improve both the ageing and the capacity of such electrodes.

**METHODS**

**Graphene Growth.** Graphene sheets were grown on electropolished copper (Cu) foils, using the procedure described in ref 44. Briefly, raw Cu foils (NILACO, 99.96% purity, 100 μm thick) were rinsed with acetone, isopropyl alcohol, and ethanol before being preannealed at 1050 °C for 2 h, under a pressure of 500 Torr in a mixture of Ar (100 sccm) and H₂ (10 sccm) atmosphere. Following this first annealing, electropolishing of the Cu foils was performed at a current density of 380 mA/cm² in a 2.17 M H₂PO₃ electrolyte, mixed with ethylene glycol at a temperature of 65–68 °C. After careful rinsing and drying, the electropolished Cu foils were loaded in a hot wall CVD reactor consisting of a 2 in. diameter horizontal quartz tube enclosed in a cylindrical furnace and pumped by a rotary pump. The Cu foils were then post-annealed at 1000 °C in a H₂ flow (30 sccm) under a pressure of 0.2 Torr for 10 min, followed by graphene growth at 1000 °C, under a pressure of 0.25 Torr with a CH₄ (20 sccm)/H₂ (2 sccm) mixture, for 30 min.

**Graphene Etching; Fabrication of NPG Membranes.** The etching of individual graphene sheets, to obtain nanoporous graphene (NPG) was performed immediately after growth (i.e., before transfer onto the Al-based anode). NPG was obtained by etching graphene sheets in a DIENER low pressure O₂ plasma generator (ZEPTO model, version B), following the method reported by Lee et al. To avoid direct ion bombardment during the etching process, the samples were placed face down in the plasma reactor and they were supported by an ~1 mm-high metallic spacer (Figure 7). The optimum etching conditions were found by keeping the O₂ pressure and flow constant (30 sccm, 0.1 bar), while varying the power (from 6 to 20 W) and the etching time (from 0.5 to 5 s).

**Graphene and NPG Transfer onto Si/SiO₂ Substrates.** For Raman characterization, the graphene sheets were first transferred onto oxidized Si substrates. Poly(methyl methacrylate) (PMMA) diluted in 4% anisole (Microchem, 950 PMMA, A4) was spin-coated on graphene/Cu foils and soft-baked for 2 min at 70 °C. Graphene grown on the rear side of Cu foils was then removed by O₂ plasma etching (A-Tec ICP-RIE reactor, 170 mTorr, 10 W, 60 s). Next, the Cu substrate was etched away using a FeCl₃-based copper etchant (CE-100, TRANSENE) for 40 min at room temperature. After rinsing for 1 h in deionized water, the PMMA/graphene films were transferred onto SiO₂ (300 nm)/Si substrates. The PMMA layer was then removed in hot acetone (Sigma-Aldrich, no. 270725, 99.9%) at 50 °C, for 3 h.

**NPG Transfer onto Al Thin Films.** Following plasma treatment, the NPG samples were coated with PMMA and the Cu substrate etched away as above (FeCl₃, for 40 min). After careful rinsing, the PMMA/graphene films were transferred onto the Al thin films (previously deposited on Cu current collectors) and the PMMA layer was removed in hot acetone. And then, the samples were annealed in a furnace for 2 h at 200 °C to remove the air trapped at the interface between NPG and Al thin films and to improve contacts with each other.

**Raman Characterization.** The Raman characterization of graphene and NPG membranes was performed using a Renishaw, RM1000 microprobe Raman spectrometer, at an excitation wavelength of 532 nm. For all the observations reported here, the samples, whether graphene or NPG, were first transferred on oxidized Si substrates.

**Electron Microscope Observations.** Scanning electron microscope observations were performed with a JEOl JSM 7600F instrument. Transmission electron microscope (TEM) observations were performed inside a JEOL JEM ARM 200F TEM operating at 80 (for graphene observation) or 200 kV and equipped with a Cs image corrector.

**X-ray Diffraction Analysis.** X-ray diffraction analysis were performed using a Smartlab (serial number being JD3643N) instrument with an X-ray generator power of 9 kW and a range between 15 and 80° with a scan rate of 1°/min. Prior to X-ray diffraction measurements, the samples were prepared as explained below:

The samples were taken out of the battery cell after battery testing inside a glove box. They were covered twice by nail varnish diluted with a small amount of acetone (1:10 ratio) by spin-coating (5000 rpm for 2 min) inside the glove box. This procedure guarantees no air exposition during the recording of X-ray spectra.

**Electrochemical Testing.** Anodes consisting of NPG/Al composites deposited on electropolished Cu current collectors were mounted into Swagelok-type cells for electrochemical testing (see Figure S1, Supporting Information). Metallic Li foils (Sigma-Aldrich, 99.9% purity, 0.38 mm thickness) were used as counter electrodes in the so-called half-cell configuration. The separators were 25 μm thick SELGARD 2500 microporous monolayer polypropylene membranes and the electrolyte (Soulbrain Co., Ltd., South Korea) consisted of a 1 M LiPF₆ solution diluted in a 1:1 (vol %) mixture of ethylene carbonate and dimethyl carbonate. The cell separators were saturated by a few drops of electrolyte when the cell is mounted.

To determine the precise mass of Al, each sample was carefully weighed (before and after Al deposition) by using an A&D BM-22 microbalance (A&D Company Ltd., Japan) with a sensitivity and precision of 1 μg.

The electrochemical behavior of the electrodes was investigated with a battery tester system (Bio-Logic VSP, from Bio-Logic Science Instruments SAS, France) using various charge–discharge rates. Galvanostatic cycling was performed using a voltage window between 3 and 0 V vs Li/Li⁺. Cyclic voltammetry was performed between 2 and 0 V (vs Li/Li⁺) at a scanning rate of 0.05 mV/s. We have taken 1400 mAh/g as the nominal Al capacity for the determination of the C rates.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b08358.

Anode preparation process, test battery cell assembly (Figure S1), copper foil lamination effect (Figure S2), galvanostatic plots for various number of NPG sheets (Figure S3), X-ray diffraction spectra during the first cycle (Figure S4), cyclic voltammetry plots with and without NPG (Figure S5), delithiation analysis by X-ray diffraction (Figure S6) (PDF)

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**Notes**

The authors declare no competing financial interest.

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