Research Article
Effects of Alumina Films on N-Doped Carbon Nanotubes/Graphene Composites as Anode Materials of Lithium-Ion Batteries

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A carbon nanotubes/graphene composite is grown on nickel foil without additional catalysts by one-step ambient pressure chemical vapor deposition (CVD). Next, the carbon nanotubes/graphene composite is modified by radio frequency (RF) nitrogen plasma. Finally, to improve its initial coulombic efficiency/electrochemical stability, lower potential during the charge process (coin cell), and boost potential during the discharge process (lithium-ion battery), alumina is deposited onto the N-doped carbon nanotubes/graphene composite by RF magnetron sputtering at different power levels and periods of time. The charge specific capacity (597 mAh/g) and initial coulombic efficiency (81.44% > 75.02% for N-doped carbon nanotubes/graphene) of Al₂O₃/N-doped CNTs/graphene for the coin cell reached a maximum at the best sputtering condition (power = 65 W and time = 30 min). Al₂O₃/N-doped CNTs/graphene (the best sputtering condition) exhibits higher initial coulombic efficiency (79.8%) compared with N-doped CNTs/graphene (initial coulombic efficiency: 74.3%) for the lithium-ion battery. Furthermore, the achievement fraction (about 70%) of full charge capacity (coin cell) for Al₂O₃/N-doped carbon nanotubes/graphene (the best sputtering condition) is higher than that (about 30%) for N-doped carbon nanotubes/graphene at a voltage lower than about 0.25 V. Moreover, it also shows a little higher electrochemical stability (coin cell) of charge capacity for Al₂O₃/N-doped carbon nanotubes/graphene (the best sputtering condition) in comparison with N-doped carbon nanotubes/graphene and Al₂O₃/N-doped CNTs/graphene (the best sputtering condition) exhibits better cyclic stability (lithium-ion battery) of discharge capacity compared with N-doped CNTs/graphene.

1. Introduction
The applications of lithium-ion batteries include portable electronic devices, electric vehicles, and hybrid electric vehicles. In comparison with other batteries, lithium-ion batteries have higher energy densities, higher voltage, and lower maintenance [1]. The performance of lithium-ion batteries mainly depends on the properties of anode and cathode materials. In this research, we focused on anode materials of lithium-ion batteries.

In our previous study [2], one-step ambient pressure CVD was used to simultaneously synthesize carbon nanotubes (CNTs) as well as graphene on nickel foam without additional catalysts at 800°C and then the carbon nanotubes/graphene composite was modified by RF nitrogen plasma treatment. However, it still possessed lower initial coulombic efficiency/electrochemical stability and mainly occurred higher potential during the charge process of the coin cell as well as lower potential during the discharge process of the lithium-ion battery for the N-doped carbon nanotubes/graphene composite. Therefore, to improve its initial coulombic efficiency/electrochemical stability, lower potential during the charge process of the coin cell, and enhance potential during the discharge process of the lithium-ion battery.
Figure 1: Schematic illustration of the fabrication process of Al₂O₃/N-doped CNTs/graphene.

Figure 2: Raman spectra of Al₂O₃/N-doped CNTs/graphene.
battery, the N-doped carbon nanotubes/graphene composite was modified by oxides in this research.

An alumina layer was deposited on silicon by atomic layer deposition (ALD) to prevent some side reactions between the silicon and the electrolyte, and then the coulombic efficiency and electrochemical stability were improved [3]. A smooth alumina protective layer was deposited on Al-doped (enhancing the electronic conductivity of insulating alumina) porous C/SiO₂ composites, and alumina could act as a preformed solid electrolyte

Figure 3: The FESEM image and EDX elemental mappings as well as intensities of C, O, Al, and N in Al₂O₃/N-doped CNTs/graphene (the best sputtering condition).
interface (SEI) film to decrease lithium ions consumption in the regeneration of SEI films as well as then increase the coulombic efficiency as well as electrochemical stability [4]. Alumina artificial SEI layers with different thickness which suppressed the growth of SEI films were deposited on the SnO$_2$/CNTs composite by ALD at different cycles.
and electrochemical stability, rate capability, and coulombic efficiency were improved [5]. An alumina passive layer which blocked the interaction between Fe₃O₄ and the electrolyte to prevent the formation of SEI films was deposited on Fe₃O₄-reduced graphene oxide composite by ALD, and electrochemical stability was improved [6]. Alumina coating was deposited on the MnO₂/CNTs composites by ALD, and the initial coulombic efficiency was increased with the increase of the coating thickness; however, a thick alumina film decreased the electrochemical performances by inhibiting lithium-ion intercalation [7]. To improve the initial coulombic efficiency, electrochemical stability, and high-rate performance, alumina was coated on natural graphite powder by a sol-gel method and the alumina coating could act as a preformed SEI film to allow lithium-ion transport, prevent electron transfer, and reduce the regeneration of SEI films as well as lithium ion consumption during subsequent cycling [8]. Multi-walled carbon nanotubes (MWCNTs) were directly grown on the Cu current collector by CVD, then alumina was deposited on the MWCNTs by ALD, and alumina could enhance electrochemical stability and lithium-ion intercalation capacity [9]. Alumina with different thickness was deposited on lithium metal by RF magnetron sputtering at a fixed power level (80 W) as well as different time periods (10 min-60 min), and lithium metal coated with a 20 nm thick alumina possessed better electrochemical stability than lithium metal [10]. So, alumina was deposited onto the N-doped carbon nanotubes/graphene composite by RF magnetron sputtering at different power levels and periods of time in this study.

2. Materials and Methods

We followed the methods of Lin et al. (2018) [11] and Lin et al. (2020) [12] to prepare a carbon nanotubes/graphene composite. Next, the carbon nanotubes/graphene composite was modified by nitrogen plasma according to the method of Lin et al. (2020) [12]. Finally, alumina was deposited onto the N-doped carbon nanotubes/graphene composite by RF magnetron sputtering from a 3 inch disk AI target (purity: 99.7%, purchased from Solar Applied Materials Technology Corporation, Taiwan) in a vacuum chamber with a background pressure of 7 x 10⁻⁶ torr. The distance between the target and the substrate was 8 cm. The pressure and volume flow rates of argon as well as oxygen were maintained at 20 mtorr and 25 sccm as well as 10 sccm, respectively. The power levels (50, 65, and 80 W) and time periods (5, 10, 30, 50, and 70 min) were varied.

A solution of 1 M LiPF₆ dissolved in 1:1:1 (wt%) ethylene carbonate-ethyl methyl carbonate-dimethyl carbonate from Ubiq Technology was used as the electrolyte. The anode electrode (π x 0.65 x 0.65 cm², Li metal: 99.9%, 0.3 mm thick, Ubiq Technology) was assembled with the cathode electrode (π x 0.65 x 0.65 cm², N-doped CNTs/graphene or Al₂O₃/N-doped CNTs/graphene) into a coin cell with the 0.1-0.15 ml electrolyte (1 M LiPF₆) and the PP/PE/PP separator (Celgard 2325, Celgard, USA) at room temperatures (about 293-303 K) by using a coin cell manual crimping machine (CR2032, Taiwan) in an Ar-filled glove box. Furthermore, the cathode electrode (π x 0.65 x 0.65 cm², LiCoO₂; 92% of purity, Ubiq Technology) was assembled with the anode electrode (π x 0.65 x 0.65 cm², Al₂O₃/N-
doped carbon nanotubes/graphene composites (the best sputtering condition) into a lithium-ion battery (full cell) with the same procedure as the coin cell. The electrochemical cycling tests were performed at 0.1-2 C with a potential range of 0.01 V to 3 V (vs. Li⁺/Li) for the coin cell (a potential range of 1-4.5 V for the full cell) using a cycler (PFX 2011, Kikusui, Japan).

The D peak, G peak, 2D peak, and Al₂O₃ peak for the Al₂O₃/N-doped carbon nanotubes/graphene composite (the best sputtering condition) were investigated by microscopic Raman spectrometer (633 nm of wavelength; in Via, Renishaw, England). Furthermore, the structure or chemical composition of Al₂O₃/N-doped CNTs/graphene for sputtering alumina onto N-doped CNTs/graphene composites at 65 W and different time periods were conducted by field emission scanning electron microscope (FE-SEM) combined with energy-dispersive X-ray (EDX) (JEOL JSM-6700F, Japan). Additional information on the surface roughness (root-mean-square (rms) got by running NanoScope Analysis using original AFM data as input) of Al₂O₃/N-doped CNTs/graphene for sputtering alumina onto N-doped CNTs/graphene composites at different power levels and time periods was obtained by atomic force microscope (AFM, Dimension ICON Bruker, Germany). Moreover, cyclic voltammetry tests of the coil cell for Al₂O₃/N-doped CNTs/graphene (the best sputtering

![Figure 7: (a) The correlation between the charge specific capacity and the roughness and (b) the correlation between the initial coulombic efficiency and the roughness.](image-url)
condition) were performed using an electrochemical analyzer (CH Instruments CHI 608B, USA) with the CR2032 coin cell over a potential range of 0.01-3.0 V at a scan rate of 0.1 mV s\(^{-1}\).

3. Results and Discussion

Figure 1 shows alumina fabricated by sputtering Al\(_2\)O\(_3\) onto the N-doped CNTs/graphene composite grown on nickel foam by CVD and treated with N\(_2\) plasma. The Raman spectra (see Figure 2) for the Al\(_2\)O\(_3\)/N-doped carbon nanotubes/graphene composite (the best sputtering condition), the peaks positioned at 1350 cm\(^{-1}\) (D), 1550 cm\(^{-1}\) (G), and 2665 cm\(^{-1}\) (2D), can be assigned to CNTs as well as graphene which also are confirmed by the FESEM images of CNTs as well as graphene sheets being simultaneously synthesized at 800°C in our previous paper [2]; the peaks located at 372.7 1/cm, 415.7 1/cm, 423.5 1/cm, 454.6 1/cm, 574.1 1/cm, and 755.5 1/cm for the E\(_{g}\) (TO), A\(_{1g}\) (LO), E\(_{g}\) (TO), E\(_{g}\) (LO), E\(_{g}\) (LO), and E\(_{g}\) (LO), respectively, can be attributed to Al\(_2\)O\(_3\) as well as are in good agreement with the previous literature [13], and the sharp peaks at about 500 1/cm and 700 1/cm are spinel \(\gamma\)-Al\(_2\)O\(_3\) as well as the sharp peak at about 620 1/cm is nonspinel \(\gamma\)-Al\(_2\)O\(_3\) [14]. Furthermore, aluminia coated onto the N-doped CNTs/graphene composite was also verified from the EDX element mappings and intensities in Figure 3 which exhibited Al and O for Al\(_2\)O\(_3\)/N-doped CNTs/graphene.

Figures 4 and 5 show the effects of power levels and time periods for sputtering alumina onto N-doped carbon nanotubes/graphene composites on the charge specific capacity (0.1 C) and initial coulombic efficiency of alumina/N-doped CNTs/graphene. The charge specific capacity (597 mAh/g) and initial coulombic efficiency (81.44%) reached a maximum at the best sputtering condition (power = 65 W and time = 30 min). The higher the surface roughness, the lower the charge specific capacity (see Figures 4 and 6) and nearly the lower the initial coulombic efficiency (see Figures 5 and 6) since a higher rough surface leads to probably increasing electrolyte decomposition, then forming more SEI, and also consuming more lithium ions during predischarging [8]. They also show that the charge specific capacity is obviously proportional to the surface roughness \((R^2 = 0.96; \text{see Figure 7(a)})\), and initial coulombic efficiency is nearly proportional to the surface roughness \((R^2 = 0.66; \text{see Figure 7(b)})\). Furthermore, the charge specific capacity increased with time periods in the range 10-30 min for 65 W of the power level. This picture
may be explained as follows. A shorter time period (10 min) leads to less Al₂O₃ deposited and forming a thinner Al₂O₃ coating (see Figure 8(a)), which might not be insulating as well as strong enough to act as a proper preformed SEI as well as reduce SEI formation during predischarging; then, charge specific capacity is lower (see Figure 4), and thus, initial

Figure 9: The discharge-charge profiles (between 0.01 V and 3 V at 0.1 C) with different charge-discharge cycles of the coin cell for (a) the N-doped CNTs/graphene composite [2] and (b) Al₂O₃/N-doped CNTs/graphene (the best sputtering condition).
coulombic efficiency is lower (see Figure 5). A longer time period (30 min) leads to more Al\textsubscript{2}O\textsubscript{3} homogeneously deposited and forming a uniform Al\textsubscript{2}O\textsubscript{3} coating layer with proper thickness (see Figure 8(b)) that could act as a preformed SEI to reduce SEI formation during predischarging; then, charge specific capacity is higher (see Figure 4), and thus, initial coulombic efficiency is higher (see Figure 5). However, the charge specific capacity decreased with time periods in the range 30-50 min for 65 W of the power level. The reason behind this may be that an overly long time period leads to

![Figure 10: Cyclic voltammograms (between 0.01 V and 3 V from the 1st cycle to the 3rd cycle) of the coin cell for (a) the N-doped CNTs/graphene composite and (b) Al\textsubscript{2}O\textsubscript{3}/N-doped CNTs/graphene (the best sputtering condition).](image-url)
an overly much Al₂O₃ deposited and forming a Al₂O₃ coating layer with over thickness (see Figure 8(c)), which could decrease lithium-ion to diffuse through it, then decreasing charge specific capacity (see Figure 4), and thus decreasing initial coulombic efficiency (see Figure 5). The above behavior is similar to the previous literature [7].

Figures 9(a) and 9(b) show the discharge-charge profiles (0.1 C) of the coin cell for N-doped CNTs/graphene and

![Graphical representation of the discharge-charge profiles for N-doped CNTs/graphene and Al₂O₃/N-doped CNTs/graphene.](image)
The appearance of the plateaus in the predischarge curve can be assigned to forming the SEI film on the surface of electrodes as well as the degrading electrolyte [15], and the predischarge plateaus rapidly disappear in the following cycles (see Figures 9(a) and 9(b)) which also are verified by the cathode peaks (about 0.6 V-0.7 V) happening during the 1st (predischarge) cycle and disappearing in the subsequent cycles (see Figures 10(a) and 10(b)).

Al₂O₃/N-doped CNTs/graphene (the best sputtering condition). The cathode peak (about 0.7 V) in the 1st (predischarge) cycle of Al₂O₃/N-doped CNTs/graphene (the best sputtering condition) is not sharper than the cathode peak (about 0.6 V) in the 1st

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**Figure 12:** The effects of the N-doped CNTs/graphene composite [2], Al₂O₃/N-doped CNTs/graphene (the best sputtering condition), and different charge-discharge cycles on the charge specific capacity (0.1 C) for the coin cell.

**Figure 13:** The effects of different charge-discharge cycles on the coulombic efficiency of Al₂O₃/N-doped CNTs/graphene (the best sputtering condition) for the coin cell.
(predischarge) cycle of N-doped CNTs/graphene (see Figures 10(a) and 10(b)) since Al₂O₃ coating layer could act as a preformed SEI to block the electrolyte, then suppress undesired side reactions with the electrolyte, and thus reduce SEI formation during predischarging. Therefore, the potential plateau in the predischarge curve of Al₂O₃/N-doped CNTs/graphene (the best sputtering condition) is not more obvious than that of N-doped CNTs/graphene and is extended over wider voltage ranges (about 1 V-0.5 V) that may be related to initial breakdown of the oxide [9]. Furthermore, an important feature of the discharge-charge profiles for Al₂O₃/N-doped CNTs/graphene (the best sputtering condition) is availability of the good fraction (about 70%) of full charge capacity at a voltage lower than about 0.25 V which is the potential plateau in the charge curves of Figure 9(b) that can be attributed to the Li⁺ deintercalation from the carbon (see Figure 10(b)) [2]. However, the fraction (about 30%) of full charge capacity at a voltage lower than about 0.25 V for N-doped CNTs/graphene is bad (see Figure 9(b)). If charge specific capacity (about 400 mAh/g) is the same, it occurs at lower potential (about 0.25 V) for Al₂O₃/N-doped CNTs/graphene (the best sputtering condition) and at higher potential (about 1.1 V) for N-doped CNTs/graphene (see Figures 9(a) and 9(b)). Therefore, the cathode electrode (LiCoO₂) was assembled with the anode electrode (Al₂O₃/N-doped carbon nanotubes/graphene (the best sputtering condition)) into the full cell and the achievement fraction (about 56%) of full discharge capacity for Al₂O₃/N-doped CNTs/graphene (the best sputtering condition) is higher than that (about 48%) for N-doped CNTs/graphene at a voltage higher than about 0.4 V (see Figures 11(a) and 11(b)). Al₂O₃/N-doped CNTs/graphene (the best sputtering condition) possessed better cyclic stability of discharge capacity and higher initial coulombic efficiency (79.8%) in comparison with N-doped CNTs/graphene (initial coulombic efficiency: 74.3%) (see Figures 11(a) and 11(b)) for the full cell since Al₂O₃ improved bonding of SEI with carbon and reduced SEI formation during predischarging [7, 9]. So, the full cell for Al₂O₃/N-doped CNTs/graphene is a little higher potential for the benefit of merchantable lithium-ion batteries.

Figure 12 shows the effects of Al₂O₃/N-doped CNTs/graphene (the best sputtering condition), N-doped CNTs/graphene, and different charge-discharge cycles on the charge specific capacity (0.1 C) for the coin cell. The charge specific capacity fading for Al₂O₃/N-doped CNTs/graphene is a little smaller than that for N-doped CNTs/graphene (see Figure 12) which also is verified by the discharge-charge profiles of N-doped CNTs/graphene and Al₂O₃/N-doped CNTs/graphene (the best sputtering condition) (see Figures 9(a) and 9(b)). Because Al₂O₃ improved bonding of SEI with carbon and then stabilized the electrode [7, 9], Al₂O₃/N-doped CNTs/graphene possessed a little better cycling performance (charge specific capacity only decreased 2.6% from the 1ˢᵗ cycle to the 2₀ᵗ cycle in Figure 12) compared with N-doped CNTs/graphene (charge specific capacity decreased 5.7% from the 1ˢᵗ cycle to the 1⁹ᵗ cycle in Figure 12). Furthermore, Figure 13 shows the effects of different charge-discharge cycles on the coulombic efficiency of Al₂O₃/N-doped CNTs/graphene (the best sputtering condition) for the coin cell. Al₂O₃/N-doped CNTs/graphene possessed higher initial coulombic efficiency (81.44%) (see...
Figure 13) in comparison with the N-doped CNTs/graphene composite (initial coulombic efficiency: 75.02%) [2] for the coin cell because Al$_2$O$_3$ reduced SEI formation during predischarging [7, 9]. The more the cycle number, the more the stable SEI film, then the smaller the differences of the coulombic efficiency between cycles (see Figure 13). Moreover, since a uniform Al$_2$O$_3$ coating layer with proper thickness could act as a preformed SEI to reduce regeneration of SEI (lithium-ion consumption) as well as then produce less SEI fragments during cycling and improved bonding of SEI with carbon as well as then stabilized the electrode [7, 9], Al$_2$O$_3$/N-doped CNTs/graphene (the best sputtering condition) compared with N-doped CNTs/graphene exhibited better rate performance at relatively high current density (0.5 C–2 C) for the coin cell (see Figure 14) which is similar to the previous literature [8].

4. Conclusions

The longer the time period in the range 10–30 min for 65 W of the power level, the higher the charge specific capacity (coil cell). However, the longer the time period in the range 30–50 min for 65 W of the power level, the lower the charge specific capacity (coil cell). Furthermore, at a voltage higher than about 0.4 V, the achievement fraction (about 56%) of full discharge capacity (lithium-ion battery) for Al$_2$O$_3$/N-doped CNTs/graphene (the best sputtering condition) is higher than that (about 48%) for N-doped CNTs/graphene. Moreover, Al$_2$O$_3$/N-doped CNTs/graphene (the best sputtering condition) compared with N-doped CNTs/graphene possessed better rate performance at relatively high current density (0.5 C–2 C) for the coin cell.

Data Availability

Data of Raman, discharge/charge, and CV are available.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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