Carbon Nanotubes/Graphene Composites Treated by Nitrogen-Plasma and Covered with Porous Cobalt Oxide through Galvanostatic Electrodeposition as well as Annealing for Anode Materials of Lithium-Ion Batteries

Chuen-Chang LIN,* An-Na WU, and Shun-Hong JIANG

Department of Chemical & Materials Engineering, National Yunlin University of Science and Technology, 123 University Road Sec. 3, Douliu, Yunlin 64002, Taiwan

*Corresponding author: linchuen@yuntech.edu.tw

ABSTRACT

Carbon nanotubes/graphene composites are grown on nickel foil without additional catalysts by chemical vapor deposition. Next, to improve the anchoring and uniform dispersing of Co(OH)₂ onto carbon nanotubes/graphene composites, the carbon nanotube/graphene composites are modified by radio frequency nitrogen-plasma. Then porous Co(OH)₂ thin films are galvanostatically electrodeposited onto N-doped carbon nanotubes (CNTs)/graphene composites at different currents and time periods. Finally, the porous Co(OH)₂ is transformed into porous Co₃O₄ by annealing. The charge specific capacity (1290 mAh g⁻¹) reaches a maximum at the galvanostatic electrodeposition condition (current = 1.5 mA and time = 300 s) for the coin cell. Furthermore, Co₃O₄/N-doped CNTs/graphene possesses higher charge (discharge) specific capacity and better electrochemical stability in comparison to Co₃O₄/CNTs/graphene for the coin cell (full cell: i.e. lithium-ion battery).

Keywords : Porous Co₃O₄/N-doped CNTs/graphene, Nitrogen-plasma, Galvanostatic Electrodeposition, Lithium-ion Batteries

1. Introduction

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 depend on the properties of anode and cathode materials. The anode materials of lithium-ion batteries were focused in this study.

To synthesize carbon nanotubes (CNTs)/graphene composites, in our previous studies,²³ CNTs/graphene composites were directly grown on cobalt catalysts-coated nickel foam by one-step ambient pressure chemical vapor deposition (CVD) at different temperatures and times to control the packing density of CNTs and the number of graphene layers; to simultaneously synthesize CNTs as well as graphene on nickel foam without additional catalysts, one-step ambient pressure CVD was used to grow them at different temperatures and CNTs as well as graphene were simultaneously synthesized by CVD at 800°C. Therefore, carbon nanotubes/graphene composites were synthesized by CVD at 800°C in this research.

Co₃O₄ nanocrystals uniformly distributed on N-doped reduced graphene oxide by the hydrothermal reaction method due to the doped nitrogen atoms acting as crucial anchoring sites for Co₃O₄ nucleation and thus being helpful for in situ growth of Co₃O₄ exhibited good rate capability.¹¹ Nanosized Co₃O₄ uniformly dispersed at the edge and basal plane of nitrogen-modified (by microwave exfoliating) graphite oxide possessed high reversible capacity and low first irreversible loss due to the anchoring effect of N (pyridinic and pyrrolic N being advantageous for the Co₃O₄ growth) being effective in reducing the concentration of oxygen-containing functional groups.¹² The N functional groups on carbon materials react with Li to produce LiₓN, which can react with Co to form CoₓN that can further react with Li to produce LiₓCoₓ₋₁N for promising the anode with good cyclic life and high capacity.¹³ The chemical and electronic coupling of graphite carbon nitride and N-doped graphene could be helpful for the anchoring and uniform dispersing of Co₃O₄ nanocrystals; the composite displayed high specific reversible capacity, excellent cyclic stability and rate capability.¹⁴ N-doped graphene can hybridize with other materials as the electrodes of lithium-ion batteries and the N-doped graphene has three advantages for the construction of hybrid materials: firstly, it prevents the aggregation of nanoparticles and thus providing more contact areas (active sites) between the nanoparticles as well as electrolyte; secondly, it enhances the electrical conductivity (note: this is depending on the doping level; if there is too much N, the electrical conductivity will drop due to breakdown of carbon structure) and increases the electron transfer; thirdly, it contributes certain discharge capacitances due to inducing defects as well as enlarging lattice spacing between graphene layers and binds well with inorganic nanoparticles as well as thus well maintains the integrity/stability of electrode materials.¹⁵ Thus, to improve the anchoring and uniform dispersing of Co(OH)₂ onto carbon nanotubes/graphene composites, the carbon nanotube/graphene composites were modified by radio frequency (RF) nitrogen-plasma in this study.

Hierarchical porous Co₃O₄ array films fabricated by galvanostatic electrodeposition through polystyrene sphere template followed by annealing exhibited high capacity and good cyclic stability.¹⁶ Three dimensional macroporous/porous Co₃O₄ nanosheet arrays prepared by galvanostatic electrodeposition followed by annealing displayed high reversible capacity, ultrahigh rate capacity, and excellent cyclic life.¹⁰ Porous Co₃O₄ nanostructured thin films with high porosity as well as surface area prepared by galvanostatic electrodeposition followed by annealing possessed high capacity and cyclic stability.¹¹ Therefore, to obtain porous Co₃O₄ thin films with high porosity and surface area, Co₃O₄ thin films were prepared by galvanostatic electrodeposition followed by annealing in this research.

The main aim of this research was to improve the characteristics of anode materials of lithium-ion batteries through modifying carbon nanotube/graphene composites by RF nitrogen-plasma, then...
galvanostatically electrodepositing porous Co(OH)₂ thin films onto N-doped carbon nanotubes/graphene composites at different currents as well as time periods and transforming Co(OH)₂ into Co₃O₄ by annealing.

2. Experiment

Nickel foam with three-dimensional conductive network structure working as template for the growth of graphene facilitated easy access of electrolyte ions to the electrode surface.¹₂,¹³ The use of Ni foam is known to increase the active material utilization of the electrode, and thus the specific capacitance of the electrode with the Ni foam current collector is higher than that with the Ti mesh current collector, which is similar to Ni sheet current collector. The Nickel foam (π × 0.65 × 0.65 × 0.1 cm²) was degreased ultrasonically (40 kHz) in acetone for 15 min. Then, it was rinsed ultrasonically (40 kHz) with pure de-ionized water for 15 min, and then oven-dried in air (50°C) to constant weight.

First, the pretreated nickel foam substrate was heated at 1000°C in H₂ (100 sccm) and Ar (250 sccm) for 10 min to reduce the surface oxide layer. Next, carbon nanotubes/graphene composites were directly and simultaneously synthesized on the annealed nickel foam without additional catalysts using one-step ambient pressure thermal CVD with a gas mixture of C₂H₂ (15 sccm), H₂ (100 sccm), as well as Ar (250 sccm) for 10 min at 800°C and then cooled to ambient temperatures in Ar with the same volume flow rate as carbon nanotubes/graphene composites grown. Finally, the carbon nanotubes/graphene composites were weighted.

The carbon nanotubes/graphene composites were placed in the reaction chamber (85 cm³) of the apparatus for RF plasma treatment (frequency: 13.56 MHz and maximum power: 1000 W). Next, the chamber was vacated to 10⁻¹⁰ to 10⁻¹⁰ mbar. Next, 20 sccm of nitrogen gas and 10 sccm of argon gas were introduced to the chamber to maintain its pressure at 0.174 mbar. Finally, adding nitrogen-doped defects to the surface of the carbon nanotube/graphene composites, the carbon nanotube/graphene composites were modified by nitrogen-plasma at 100 W for 15 min and then reweighed.

The porous Co(OH)₂ thin films were galvanostatically electro-deposited onto N-doped CNTs/graphene composites (π × 0.65 × 0.65 cm²) in the about 200 ml of 0.5 M Co(NO₃)₂ solution (Co(NO₃)₂·6H₂O (purity: 97%) dissolved in distilled water) contained in the 250 ml glass cup at room temperatures (about 293–303 K), different cathode currents (1, 1.5, and 2 mA) and time periods (100, 300, and 500 s) using an electrochemical workstation (CH Instruments CHI 608B, USA). Then Co(OH)₂ was transformed into Co₃O₄ by annealing at 300°C in air for 1 h.

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 × 0.65 × 0.65 cm², Li metal: 99.9%, 0.3 mm thick, Ubiq Technology) was assembled with the cathode electrode (π × 0.65 × 0.65 cm², CoO₂/CNTs/graphene or Co₃O₄/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 glovebox. The electrochemical cycling tests were performed at 0.1–2 C using a cycler (PFX 2011, Kikusui, Japan). The unit of specific capacity is mAhg⁻¹, where “g” is mass of the sum of Co₃O₄, CNTs, and graphene since we are concerned principally with the electrode made by Co₃O₄, CNTs, and graphene.

The Co 2p peaks of Co₃O₄ for the Co₃O₄/N-doped carbon nanotubes/graphene composites [the best electrodeposition condition: current = 1.5 mA and time = 300 s for galvanostatically electrodoping Co(OH)₂ onto N-doped carbon nanotubes/graphene composites] were explored by XPS (Fison VG, ESCA210, England). The D peak, G peak, 2D peak, and Co₃O₄ peak for the Co₃O₄/N-doped carbon nanotubes/graphene composites (the best electrodeposition condition) were investigated by microscopic Raman spectrometer (633 nm of wavelength; inVia, Renishaw, England). Furthermore, the structure or the chemical composition of N-doped CNTs/graphene, CoO₂/CNTs/graphene (the best electrodeposition condition), and Co₃O₄/N-doped CNTs/graphene for Co(OH)₂ being galvanostatically electro-deposited onto N-doped CNTs/graphene composites at 1.5 mA as well as 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 Co₃O₄/N-doped CNTs/graphene being galvanostatically electro-deposited onto N-doped CNTs/graphene composites at different currents and time periods was obtained by atomic force microscope (AFM, Dimension ICON Bruker, Germany). Moreover, impedance measurement was performed using an electrochemical analyzer (CH Instruments CHI 608B, USA) with the CR2032 coin cell at a scan rate of 0.1 mV s⁻¹ and room temperatures (about 293–303 K).

3. Results and Discussion

Cobalt oxide fabricated by galvanostatically electrodepositing Co(OH)₂ onto N-doped CNTs/graphene grown on Ni foil by CVD as well as treated with N₂-plasma and then Co(OH)₂ transformed into cobalt oxide by annealing are shown in Fig. 1. The Co 2p XPS spectrum (See Fig. 2) of the CoO₂/N-doped carbon nanotubes/graphene composites (the best electrodeposition condition) demonstrates two peaks positioned at 780.2 eV (Co 2p₁/₂) and 795.4 eV (Co 2p₃/₂) with the presence of Co(II) and Co(III).¹⁴,¹⁵ which illustrate the existence of the mixed oxidation state oxide i.e. Co₃O₄ in the composites. Furthermore, in the Raman spectra (See Fig. 3) for the Co₃O₄/N-doped carbon nanotubes/graphene composites (the best electrodeposition condition), the peaks located at 1350 cm⁻¹ (D), 1596 cm⁻¹ (G), as well as 2669 cm⁻¹ (2D) can be appointed to carbon nanotubes 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 and the peaks positioned at 190 cm⁻¹, 482 cm⁻¹, 526 cm⁻¹, 613 cm⁻¹, as well as 684 cm⁻¹ can be assigned to the F₁g, E₂¹g, F₂g, F₄g, A₁g of Co₃O₄ which is in good agreement with the previous literature.¹⁶ The I_D/I_G for CoO₂/N-doped CNTs/graphene is about equal to 1.65 (See Fig. 3). Then, the layer number of the graphene is about calculated by the equation [I_D/I_G = 0.14 + n/10], where n is the layer number of the graphene.¹⁷ The thickness of single-layer graphene is about 0.34 nm and the interlayer distance between the graphene sheets is about 0.34 nm.¹⁹ According to the above data, the thickness (9.86 nm) of the graphene can be estimated. Moreover, Co₃O₄ coated on N-doped CNTs/graphene was also verified by comparing the FESEM image in Fig. 4 with the FESEM image in Fig. 5(b). Furthermore, nitrogen doped on CNTs/graphene was verified by comparing the EDX elemental intensities in Fig. 6 which showed the N peak for Co₃O₄/N-doped CNTs/graphene.
Figure 1. Schematic illustration of the fabrication process of Co₃O₄/N-doped CNTs/graphene composites.

Figure 2. XPS spectra in Co 2P region for Co₃O₄/N-doped CNTs/graphene.

Figure 3. Raman spectra of Co₃O₄/N-doped CNTs/graphene.

Figure 4. The FESEM images of N-doped carbon nanotubes/graphene composites.

Figure 5. The FESEM images of Co₃O₄/N-doped CNTs/graphene with the current (1.5 mA) and different time periods (a): 100 s, (b): 300 s, and (c): 500 s for galvanostatically electrodepositing cobalt onto N-doped CNTs/graphene.
nitrogen atoms could act as crucial anchoring sites for Co$_3$O$_4$ nucleation and thus are helpful for in situ growth of Co$_3$O$_4$ which was also verified by comparing the FESEM image in Fig. 7 with the FESEM image in Fig. 5(b).

Figure 6. The FESEM images and EDX elemental mappings as well as intensities of (a): N in Co$_3$O$_4$/CNTs/graphene (the best electrodeposition condition) and (b): N in Co$_3$O$_4$/N-doped CNTs/graphene (the best electrodeposition condition).

Figure 8 shows the effects of currents and time periods for galvanostatically electrodepositing Co(OH)$_2$ onto N-doped carbon nanotubes/graphene composites and then Co(OH)$_2$ transformed into cobalt oxide by annealing on the specific charge capacity (0.1 C) of
Co$_3$O$_4$/N-doped CNTs/graphene for the coin cell. The charge specific capacity ($1290 \text{ mAh g}^{-1}$) reached a maximum at the galvanostatic electrodeposition conditions (current = 1.5 mA and time = 300 s). The higher the surface roughness, the higher the charge specific capacity (See Figs. 8 and 9) because a higher rough surface has larger surface area. Furthermore, the charge specific capacity increased with time periods in the range 100–300 s for 1.5 mA of the current. The reason behind this may be that a longer time period leads to more particles homogeneously deposited [See Fig. 5(a) and 5(b)], and thus enhances surface roughness (See Fig. 9) as well as charge specific capacity (See Fig. 8). However, the charge specific capacity decreased with time periods in the range 300–500 s for 1.5 mA of the current. This picture may be explained as follows. An overly long time period leads to an overly many particles deposited, which causes more particles coagulated [See Figs. 8(b) and 5(c)], then decreasing surface roughness (See Fig. 9), and thus decreasing charge specific capacity (See Fig. 8).

Figures 10(a) and 10(b) show the discharge/charge profiles (0.1 C) of the coin cell for Co$_3$O$_4$/CNTs/graphene (the best electrodeposition condition) and Co$_3$O$_4$/N-doped CNTs/graphene (the best electrodeposition condition). The appearance of the plateaus in the first discharge curve can be assigned to forming the solid electrolyte interface (SEI) film on the surface of electrodes and the discharge plateaus disappear in the following cycles [See Figs. 10(a) and 10(b)] which also is verified by the cathode peaks (about 0.8 V) happening during the first discharge cycle and disappearing in the subsequent cycles [See Figs. 11(a) and 11(b)]. The discharge specific capacity (about 770 mAh g$^{-1}$) of the plateau in the first discharge curve for Co$_3$O$_4$/N-doped carbon nanotubes/graphene composites (the best electrodeposition condition) is higher than the discharge specific capacity (about $660 \text{ mAh g}^{-1}$) of the plateau in the first discharge curve for Co$_3$O$_4$/carbon nanotubes/graphene composites (the best electrodeposition condition) because of the N-doping improving dispersion of Co$_3$O$_4$. The N-doping improved dispersion of Co(OH)$_2$ during galvanostatic electrodeposition since CNTs/graphene was transformed from the hydrophobic nature (contact angle about 108°).
to the hydrophilic nature (contact angle about 71°) after nitrogen-plasma treatment. Then Co(OH)₂ was transformed into Co₃O₄ by annealing and thus the N-doping improved dispersion of Co₃O₄. The coulombic efficiency is less than 100% for cycles 2 and later [See Figs. 10(a) and 10(b)] since Co is not likely completely re-oxidized to Co₃O₄ in the following Eq. (1).22 The more the cycle number, the higher the coulombic efficiency [See Figs. 10(a) and 10(b)] because the more the cycle number, the smaller the particle size of Co23 which leads to the larger proportion of the total number of Co lying near or on Li₂O and further makes the electrochemical reactivity of Co more.24 Furthermore, the cathode electrode (³©0.65©0.65 cm², LiCoO₂: 92% of purity and about 145 mAh g⁻¹ of specific capacity, Ubiq Technology) was assembled with the anode electrode (³©0.65©0.65 cm², Co₃O₄/carbon nanotubes/graphene composites (the best electrodeposition condition) or Co₃O₄/N-doped carbon nanotubes/graphene composites (the best electrodeposition condition)) into a lithium-ion battery (full cell) with the 0.1–0.15 ml electrolyte (1 M LiPF₆) as well as 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 and Co₃O₄/N-doped CNTs/graphene possessed higher discharge specific capacity as well as better cyclic stability in comparison with Co₃O₄/CNTs/graphene [See Figs. 12(a) and 12(b)] due to the N-doping improving dispersion of Co₃O₄ as well as strengthen interactions through Co-N-C bonds.5–8,25 The coulombic efficiency of the full cell for Co₃O₄/N-doped CNTs/graphene is higher than that for Co₃O₄/CNTs/graphene [See Figs. 12(a) and 12(b)] since the N-doping could reduce the concentration of oxygen-containing functional groups, which have higher reactivity toward the electrolytes as well as Li ions, and hence suppress the decomposition of the electrolytes to form a SEI film.4,5 If discharge specific capacity (about 600 mAh g⁻¹) of the full cell at the 1st cycle is the same, it occurs at a little higher potential (about 3.9 V) for Co₃O₄/N-doped CNTs/graphene and at a little lower potential (about 3.6 V) for Co₃O₄/CNTs/graphene [See Figs. 12(a) and 12(b)] since the crystallinity of carbon nanotubes/graphene composites increases after they being modified by nitrogen-plasma; however, the discharge processes of the full cell for Co₃O₄/N-doped CNTs/graphene happen at a little higher potential for the benefit of merchantable lithium-ion batteries. The specific capacity of the full cell is underestimated since specific capacity (about 145 mAh g⁻¹) of LiCoO₂ is not excess. Finally, Fig. 13 shows the cyclic voltammograms of the full cell for Co₃O₄/N-doped CNTs/graphene. The peaks were observed from 2.6 V to 3 V (See Fig. 13) which can be assigned to the lithiation of Co₃O₄ as well as delithiation of LiCoO₂ during the charge processes and the peak was seen at about 1.9 V (See Fig. 13) which can arise from the lithiation of Li₁₋ₓCoO₂ as well as delithiation of Co/Li₂O during the discharge processes.26,27 The charge/discharge reactions of Co₃O₄, carbon nanotubes/graphene composites, LiCoO₂, and N functional groups on carbon...
nanotubes/graphene composites can be described by Eqs. (1), (2), (3), (4), (5), (6), and (7):\(^2\)

\[
\begin{align*}
\text{Co}_3\text{O}_4 + 8 \text{Li}^+ + 8 \text{e}^- &\rightarrow 3 \text{Co} + 4 \text{Li}_2\text{O} \quad (1) \\
6 \text{C} + x \text{Li}^+ + x \text{e}^- &\rightarrow \text{C}_x\text{Li}_y \quad (2) \\
\text{LiCoO}_2 &\rightarrow \text{Li}_{1-x}\text{CoO}_2 + x \text{Li}^+ + x \text{e}^- \quad (0 \leq x \leq 1) \quad (3) \\
3 \text{Li} + \text{N} &\rightarrow \text{Li}_3\text{N} \quad (4) \\
4 \text{Co} + \text{Li}_3\text{N} &\rightarrow \text{Co} + \text{Co}_2\text{N} + 3 \text{Li} \quad (5) \\
\text{Co}_x\text{N} + x \text{Li}^+ &\rightarrow \text{Li}_x\text{Co}_{3-x}\text{N} + x \text{Co} \quad (6) \\
\text{Li}_x\text{Co}_{3-x}\text{N} + (3 - x) \text{Li} &\rightarrow (3 - x) \text{Co} + \text{Li}_3\text{N} \quad (7)
\end{align*}
\]

The main reaction \([\text{Co}_3\text{O}_4 + 8 \text{Li}^+ + 8 \text{e}^- \rightarrow 3 \text{Co} + 4 \text{Li}_2\text{O}]\) is for the high specific capacity. The reaction \([6 \text{C} + x \text{Li}^+ + x \text{e}^- \rightarrow \text{C}_x\text{Li}_y (2)]\) is for the reactions of SEI film with \(\text{Li}^+\).

Figure 14 shows the effects of \(\text{Co}_3\text{O}_4/\text{CNTs}/\text{graphene}\) (the best electrodeposition condition), \(\text{Co}_3\text{O}_4/\text{N-doped CNTs}/\text{graphene}\) (the best electrodeposition condition), and different charge-discharge cycles on the charge specific capacity (0.1 C) and coulombic efficiency for the coin cell. The reason behind this may be that electrolyte was decomposed and then a SEI film was formed after the first cycle.\(^2\) Because the N-doping could reduce the concentration of oxygen-containing functional groups, which have higher reactivity toward the electrolytes as well as Li ions, and hence suppress the decomposition of the electrolytes to form a SEI film,\(^4,5\) the charge specific capacity fading after the first cycle for \(\text{Co}_3\text{O}_4/\text{N-doped CNTs}/\text{graphene}\) is smaller than that for \(\text{Co}_3\text{O}_4/\text{CNTs}/\text{graphene}\) (See Fig. 14) which also is verified by the discharge/charge profiles of \(\text{Co}_3\text{O}_4/\text{CNTs}/\text{graphene}\) and \(\text{Co}_3\text{O}_4/\text{N-doped CNTs}/\text{graphene}\) (See Figs. 10(a) and 10(b)) and thus the coulombic efficiency for \(\text{Co}_3\text{O}_4/\text{N-doped CNTs}/\text{graphene}\) is higher than those for \(\text{Co}_3\text{O}_4/\text{CNTs}/\text{graphene}\), however, the more the cycle number, the lower the concentration of oxygen-containing functional groups, then the smaller the differences (the more stable SEI film) of the coulombic efficiency between \(\text{Co}_3\text{O}_4/\text{CNTs}/\text{graphene}\) and \(\text{Co}_3\text{O}_4/\text{N-doped CNTs}/\text{graphene}\) (See Fig. 14). Since the N-doping could improve dispersion of \(\text{Co}_3\text{O}_4\) and strengthen interactions through Co-N-C bonds,\(^5,8,23\) \(\text{Co}_3\text{O}_4/\text{N-doped CNTs}/\text{graphene}\) possessed higher charge specific capacity in comparison to \(\text{Co}_3\text{O}_4/\text{CNTs}/\text{graphene}\) and a little better cycling performance (charge specific capacity only decreased 9% from the 2nd cycle to the 50th cycle in Fig. 14) compared with \(\text{Co}_3\text{O}_4/\text{CNTs}/\text{graphene}\) (charge specific capacity decreased 16% from the 2nd cycle to the 50th cycle in Fig. 14), which also can be explained by the coulombic efficiency [See Fig. 14] and verified by the discharge/charge profiles of \(\text{Co}_3\text{O}_4/\text{CNTs}/\text{graphene}\) and \(\text{Co}_3\text{O}_4/\text{N-doped CNTs}/\text{graphene}\) [See Figs. 10(a) and 10(b)]. Furthermore, \(\text{Co}_3\text{O}_4/\text{N-doped CNTs}/\text{graphene}\) exhibits better rate capability compared with \(\text{Co}_3\text{O}_4/\text{CNTs}/\text{graphene}\) at different C-rates for the coin cell [See Fig. 15] because the charge-transfer resistance (33.2 ohm) for \(\text{Co}_3\text{O}_4/\text{N-doped CNTs}/\text{graphene}\) is lower than that (42.2 ohm) for \(\text{Co}_3\text{O}_4/\text{CNTs}/\text{graphene}\) [See Figs. 16(a) and 16(b)], suggesting that \(\text{Co}_3\text{O}_4/\text{N-doped CNTs}/\text{graphene}\) exhibits faster charge-transfer during the lithium-ion insertion/extraction reaction which is similar to the previous literatures.\(^4,5,7\) \(\text{Co}_3\text{O}_4/\text{N-doped CNTs}/\text{graphene}\) nearly returns to its original charge specific capacity when the C-rate is back to the initial 0.1 C after 25 cycles, however, \(\text{Co}_3\text{O}_4/\text{CNTs}/\text{graphene}\) shows clear charge specific capacity decline. The coulombic efficiency for \(\text{Co}_3\text{O}_4/\text{N-doped CNTs}/\text{graphene}\) is also higher than that for \(\text{Co}_3\text{O}_4/\text{CNTs}/\text{graphene}\) [See Fig. 15] since N-doping could reduce the concentration of oxygen-containing functional groups and hence suppress the decomposition of the electrolytes to form a SEI film.\(^5,5\)
4. Conclusions

The amounts of Co and O components in Co₃O₄/N-doped CNTs/graphene were more than those in Co₃O₄/CNTs/graphene. Furthermore, the charge specific capacity increased with time periods in the range 100–300 s for 1.5 mA; however, the charge specific capacity decreased with time periods in the range 300–500 s for 1.5 mA. Moreover, discharge processes of the lithium-ion battery (full cell) for Co₃O₄/N-doped CNTs/graphene happen at a little higher potential for the benefit of merchandising. Finally, Co₃O₄/N-doped CNTs/graphene shows better rate capability compared with Co₃O₄/CNTs/graphene at different C-rates.

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