High rate and high capacity lithiation of rGO-coated $\text{Co}_2(\text{OH})_2\text{CO}_3$ nanosheet arrays for lithium-ion batteries through the involvement of CO_3^{2-}

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Abstract

RGO-coated $\text{Co}_2(\text{OH})_2\text{CO}_3$ nanosheet arrays, mixed with a few CoO nanowires, were synthesized and deposited on copper foil directly via a simple one-step hydrothermal procedure. Benefited from its unique chemical composition and spatial structure, the obtained samples exhibited high performance as anode material for Lithium ion batteries, which delivered a very high reversible capacity of 2,100 mAh g⁻¹ at 100 mA g⁻¹ after activation and even as high as 1,240 mAh g⁻¹ at a much higher charge/discharge current of 5,000 mA g⁻¹. Additionally, the composite electrode exhibited a high cycling stability, 85% of the initial capacity was remained after 100 cycles test at 1,000 mAh g⁻¹. HRTEM analysis indicated that CO_3^{2-} was involved into

the energy storage process, which should be the key factor of such high capacity, while the covered layer of rGO and the synthesis route of directly deposition were suspected to play very important roles on the high stability and high power density.

Keywords: Nanocomposites; rGO-coated $\text{Co}_2(\text{OH})_2\text{CO}_3$; Lithium ion batteries

1. Introduction

Lithium ion batteries (LIBs), one of the foremost electrical energy storage devices, are now widely used in various electronic equipments and totally changed the way of our life since its commercialization. With the rapid development of hybrid electric vehicles (HEVs), electric vehicles (EVs) and various electricity-consuming intelligent devices, electrical energy storage technique will play a more vital role in the future than at any time past by. Undoubtedly, lithium ion batteries with higher energy density, higher rate capability and longer cycling stability are becoming more and more important not only for the researchers but also the ever-enlarging markets. However, the low theoretical capacity (372 mAh g^{-1}) and other drawbacks (e.g. safety, due to the formation of Li dendrite) existed in graphite [1, 2], the most widely used anode material, will surely not satisfy the future application of lithium ion batteries in a wider range. Therefore, the demand to increase the power and the energy density for advanced energy storage devices has triggered the exploration of new anode materials with higher theoretical capacity and better electrochemical performance.

Among numerous alternative materials, transition metal oxides (TMOs) have been reckoned as one of the most promising candidates to replace the graphite anode for LIBs due to their high theoretical capacity, high safety, easy synthesis and so on. Unlike graphite which can store one Li atom in every six carbon atoms at very low voltage, TMOs undergo a conversion reaction mechanism where lithium ions can reversibly react with the metal oxides to form Li_2O at higher voltage ($\sim 1\text{V}$ vs. Lithium)

[3]. As common multivalent materials, cobalt oxides as well as other cobalt based compounds have drawn extensive interest not only for SCs [4] but also for LIBs due to their high theoretical capacity (e.g. CoO, 716 mAh g⁻¹; Co₃O₄, 890 mAh g⁻¹) [5, 6], which are several times higher than those of carbonaceous materials. Recently, transition metal carbonate-based electrodes have also come into the view due to their super high theoretical capacity [7, 8]. However, the practical application of cobalt-based anodes is still a challenge because of their poor cycling performance and rate performance caused by the poor electrical conductivity and the large volume change during charge/discharge [9]. Hence, advances in the electrochemical performance of those materials are being achieved by several strategies, including nanostructuring, morphological optimization, surface coating, doping, and compounding [10], and some significant progress has been made. To date, numerous nanostructured cobalt-based anode materials, such as nanowires [5, 11], nanotubes [12, 13], nanorods [14-16], nanosheets [17, 18], hollow spheres [19-21], as well as their composite with graphene [22-26] have been synthesized and investigated extensively. Furthermore, construction of two or more TMOs' composite also has ever been considered for mitigating the structure collapse caused by the large volume change or the growth of grains during the charge/discharge process [27, 28].

In this work, we proposed a facile hydrothermal method to prepare cobalt hybrid oxides nanostructures, Co₂(OH)₂CO₃ nanosheet array mixed with some CoO nanowires, and covered by reduced graphene oxides (rGO) in one step with the addition of GO in the precursor solution, which were deposited on copper foil directly. The pre-added graphene oxides (GO) was partially reduced through this hydrothermal process. As parallel experiments, samples with a same procedure but no addition of GO were also prepared. The introduced rGO was well covered on the surface of active

materials, which not only acted as a substantial physical barrier to separate the $\text{Co}_2(\text{OH})_2\text{CO}_3$ nanosheets from each other but also functioned to endow the resulting composites with significantly enhanced lithium storage capability. Moreover, without the addition of binders and conductive materials but directly deposited on the current collector, cost was reduced via simplifying the craft while high electron transport was kept by the array structure along with the cross section of Cu foil. Samples with GO, without GO and of powder collected from the solution after hydrothermal reaction were denoted as S-GO, S and S-Powder, respectively. Due to the unique structural features and the synergistic effect, the S-GO electrode exhibits high capacity, good cycling stability and high rate capability when tested against a lithium metal counter electrode in a half cell. It delivered a capacity of $2,100 \text{ mAh g}^{-1}$ at 100 mA g^{-1} after activation and even as high as $1,240 \text{ mAh g}^{-1}$ at a much higher charge/discharge current of $5,000 \text{ mA g}^{-1}$, implying fast charge/discharge ability. Additionally, the composite electrode exhibited a high cycling stability, 85% of the initial capacity was remained after 100 cycles' test at $1,000 \text{ mAh g}^{-1}$ and the obvious capacity loss only focused on the first ten cycles. It was supposed that the reduced GO played a very important role in the high power density and stability. Last but not least, HRTEM analysis implies that not only Co cations, but also the anions, CO_3^{2-} , are involved into the energy storage process, which should be the key factor of such high capacity, and CO_3^{2-} can be reduced to amorphous carbon during discharge.

2. Experimental procedure

2.1. Sample synthesis

All of the chemicals used in this study were purchased from commercial sources at an analytical purity grade without any further purification. Typically, cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was added into 60 mL deionized water under vigorous

stirring to form a solution of 0.03 mol/L, then urea ($\text{CO}(\text{NH}_2)_2$) was added into the solution with a final concentration of 0.15 mol/L. After all the chemicals were fully dissolved, 1 mL GO (5 mg/mL), ultrasonicated for 20 minutes before use, was dropped into the above solution. The mixed suspension was stirred for 30 minutes and ultrasonicated for 5 minutes, and then transferred into a 90 mL Teflon-lined stainless steel autoclave. Subsequently, a piece of Cu foil ($3\text{ cm} \times 5\text{ cm}$), which was pre-cleaned ultrasonically in acetone, ethanol and deionized water for 2 minutes successively, framed with Teflon board ($3\text{ cm} \times 5\text{ cm}$, 1 mm in thickness) in either side and wrapped with Teflon tape around the board gap to prevent the reverse side from being deposited, was soaked in the solution leaning against the Teflon lining of reactor. After sealed, the autoclave was heated in an oven to $90\text{ }^\circ\text{C}$ and kept for 20 h before cooling down to room temperature naturally. Finally, the as-coated Cu foil was taken out, cleaned for several times with deionized water, dried at $80\text{ }^\circ\text{C}$ for 8 hours in a vacuum oven and named as “S-GO”. The sample “S” were prepared with the same procedure but without the addition of GO, while “S-Powder” was collected from the bottom of the autoclave for the preparation of sample “S”. When tested as half cells, all the obtained foils were cut into disc of 13 mm in diameter. The mass loading of active materials on Cu foils were measured to be $0.4\text{--}0.5\text{ mg/cm}^2$ by a microbalance (Sartorius) with an accuracy of 0.01 mg.

2.2. Characterizations

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 advance X-ray diffractometer using Cu K_α radiation ($\lambda=0.15406\text{ nm}$). Scanning electron microscopy (SEM) images were obtained using a field emission scanning electron microscope (FE-SEM, Hitachi LEO 1530). Transmission electron microscopy (TEM), selected area electron diffraction (SAED), and high-resolution TEM (HRTEM) were taken on

a JEM-2100F. Raman test was run on a Lab RAM HR Evolution system equipped with deep-depleted thermoelectrically cooled CCD array detector, an Ar laser and a long working distance 50× objective lens.

2.3. Electrochemical measurements

Electrochemical measurements were performed at 25 °C in thermostat using CR 2032-type coin cells with Celgard 2400 porous polypropylene membrane as separator, lithium-foil as both counter electrode and reference electrode and 1M LiPF₆ in EC/DMC (1:1 by volume) as electrolyte. S-Powder based electrode was prepared by making a slurry of the powder, acetylene black, and polyvinylidene difluoride (PVDF) binder (8:1:1, weight ratio) in N-methylpyrrolidone (NMP). The well-mixed slurry was then spread onto a copper foil and dried at 80 °C in a vacuum oven for 10 h to remove the water. The cells were assembled in an Ar-filled glovebox with moisture and oxygen contents both below 0.1 ppm. The discharge-charge cycling and rate performance tests of the samples were performed on a Land battery test system (CT2001A). Electrochemical impedance spectroscopy (EIS) was carried out on a Solartron electrochemical workstation (SI 1260, England) with an amplitude of 5 mV in the frequency range of 100 kHz to 0.1 Hz.

3. Results and discussion

3.1. Structure and morphology characterization

The size and morphology of the synthesized Cu foil supporting samples with and without GO were characterized by SEM and TEM first, as presented in [Fig. 1](#). It is believed that both the assembly of urea and its effects on the crystal splitting play important roles in the formation of nano-structures in the synthesis process [\[29\]](#). For the sample S-GO, with the addition of GO, separated rectangle nanosheets perpendicularly grown on the Cu substrate were obtained ([Fig. 1a](#)), which should

benefit the transmission of electrons. These nanosheets were intersecting with each other and formed 3-dimensional porous structure, which would help the fast diffusion and insertion of electrolyte ions, as well as the volume expansion during the lithiation process. More importantly, this open net-structure led to more space between each other and thus dramatically increased the specific surface area, which will provide more active sites for the Li^+ and finally enhance the performance of the electrode. When observed closely, some nanowires were found from the TEM image (Fig. 1b, the active materials were peeled off from the substrate), which is hard to be found in the SEM image due to the small amount.

In order to understand the contact surface between the active material and the Cu current collector, a cross-section SEM image was exhibited in Fig. 1c. It is clear from the figure that a thousand and one nanosheets were grown closely on the Cu foil and contacted well with it through surface powder with a deposition thickness of about 5 μm , which facilitate interfacial charge transfer and promote current collection even without the additional of conductive additives. While, sample S without GO consists of two obvious structures, nanowire and nanosheet, which piled up together on the copper foil (Fig. 1d). Meanwhile, the nanosheets were agglomeration together rather than separately. Clearly, GO played an important role in separating the nanosheets and effecting the amount ratio of nanosheets and nanowire.

According to the above morphology analysis, a simple deposition process of the samples were drafted in Fig. 2a. Meanwhile, chemical compositions of the samples were further characterized by X-ray diffraction (XRD) technology and presented in Fig. 2b. Apart from three peaks at 43.3, 50.4 and 74.1 degree which can be addressed to the Cu foil substrate (JCPDS 04-0836), the other peaks can be indexed to a mix phase of $\text{Co}_2(\text{OH})_2\text{CO}_3$ [7, 30] and CoO (JCPDS 42-1300), which should correspond

to the mix structure of nanosheets and nanowires. Even with the addition of GO during the synthesis process, no signal aroused from GO can be detected from the XRD pattern, seen from the black curve in Fig. 2b. The diffraction peak at $\sim 34.4^\circ$ can be attributed to the (012) plane of $\text{Co}_2(\text{OH})_2\text{CO}_3$, while the very weak peak nearby at $\sim 34^\circ$ can be indexed to the (111) plane of CoO. No much difference can be observed in peaks' positions of the two samples except two peaks' intensity that belong to CoO (much weaker in the sample "S-GO"), implying the addition of small quantity of GO did not change the ultimate chemical composition of the sample but the relative proportion of the two mix phases.

Since XRD can only realize rough detection to the whole sample and no peaks originated from GO can be detected, to further identify the existence of the slight GO in sample S-GO, Raman measurement that is a sensitive probe to the local atomic vibrations of nano-sized materials was operated as presented in Fig. 2c. The inset picture was a part magnification of the spectrum before 800 cm^{-1} . The bands centered at 146 cm^{-1} , 225 cm^{-1} , 485 cm^{-1} , and 685 cm^{-1} correspond to the Raman active phonon modes of CoO [31, 32]; while the bands centered at 481 cm^{-1} , 693 cm^{-1} , 730 cm^{-1} and 1070 cm^{-1} can be assigned to the Raman active modes of $\text{Co}_2(\text{OH})_2\text{CO}_3$ [33], which is consistent with the XRD results. Apparently, apart from the same bands, additional two strong bands located at 1349.3 cm^{-1} and 1599.7 cm^{-1} , which can be indexed to GO, was detected for the S-GO sample, indicating GO was indeed introduced into the sample though it cannot be detected by XRD and well distinguished by SEM.

Because of the similarity of the samples S and S-GO, HRTEM and Fast Fourier Transform (FFT) analysis were only performed to S-GO to evaluate its detailed morphological and structural features (shown in Fig. 3). Well ordered atom pattern with high crystallization can be visualized through the HRTEM image (Fig. 3b) for

S-GO, which was taken from the red square region of a nanosheet in Fig. 3a. A clear lattice fringe in the selected region can be seen obviously with d-spacing of 0.260 nm, readily indexed to the (012) plane of $\text{Co}_2(\text{OH})_2\text{CO}_3$, demonstrating that the majority nanosheet structure exhibited in above SEM image is $\text{Co}_2(\text{OH})_2\text{CO}_3$. Besides, a Fast Fourier Transform (FFT) pattern corresponding to the lattice area displayed in Fig. 3b was collected and presented in Fig. 3c, which indicates the symmetry and other lattices' information of $\text{Co}_2(\text{OH})_2\text{CO}_3$. The most distinct diffraction spots here can be assigned to (012), (400), and (401) planes of $\text{Co}_2(\text{OH})_2\text{CO}_3$. While, for the red square region taken from part of a nanowire in Fig. 3d, the adjacent fringe spacing of the aligned lattice fringes is about 0.254 nm, corresponding to the (111) plane of CoO (JCPDS 42-1300), shown in Fig. 3c. The crystallized structure is covered by an amorphous layer, which may be originated from the uncrystallized cobalt-based materials. Fast Fourier Transform (FFT) pattern of the area (Fig. 3f) clearly indicates a nature of CoO. The observable three diffraction spots were indexed to the (111), (200), and (211) planes. The d-spacing exhibited in Fig. 3b and e is quite close to each other, so it is hard to tell the phase structure if only evaluated from one lattice fringe. Hence, FFT is very necessary to further reveal all the diffraction spots and determine the crystal structure. The HRTEM analysis here is agreed well with XRD, Raman and SEM results discussed above, which demonstrate a mix structure of nanosheets and nanowires with respective phase of $\text{Co}_2(\text{OH})_2\text{CO}_3$ and CoO, respectively.

3.2. Electrochemical properties

The lithiation ability of the samples S and S-GO were evaluated based on a coin-type half-cell configuration at room temperature. Charge-discharge profiles of S and S-GO electrodes (Fig. 4a and b), as well as of a blank rGO electrode (Fig. S1), were performed between 0.01 and 3.0 V at a current density of 100 mA g^{-1} . The first

discharge and charge specific capacities were 2029.0 mAh g⁻¹ and 1495.3 mAh g⁻¹ for S sample, 2662.1 mAh g⁻¹ and 2108.9 mAh g⁻¹ for S-GO with a clear discharge voltage plateau at about 1 V. While, the contribution of rGO can be ignored due to its low amount and much lower capacity. For the first cycle, the Coulombic efficiency (charge capacity over discharge capacity) is deviated from 100%. The discharge capacities underwent an obvious drop from the first cycle to the second one, which should be addressed to the formation of SEI layer and irreversible reaction of part active materials. It can be seen clearly that both the capacity and the Coulombic efficiency of S-GO are higher than that of S, implying the advantage of separated nanosheets due to the addition of GO. CV profiles of S-GO was presented in Fig. S2. Positions and shapes of redox pairs are not stable until the fifth cycle. Two anodic peaks at about 1.3 V and 0.8 V merged to be one wide peak along with cycling. Turn-on voltage of lithiation shifted to lower position along with cycling in the first five cycles, from 1.6 V drop to about 1.2 V, which is consistent with the galvanostatic discharge curves. Large cathodic currents continue living from the turn-on voltage to off voltage, implying a continuous lithiation or a multi-electron process. In addition, the obtained capacities are much larger than the theoretical capacities of pure cobalt oxides based electrodes (e.g, CoO 716 mAh g⁻¹), which is very common in many transition-metal oxides concerned reports. The extra capacity mainly comes from the low-voltage region (below 1 V), which could be probably ascribed to interfacial lithium storage or the formation of alloy.

For carbonate based electrodes, besides the known conversion reaction of metal ions from Co²⁺ to Co⁰, C⁴⁺ in CO₃²⁻ may also participate in the electrochemical redox reactions and completely or partially reduced to C⁰ or lower valence Li_xC [34]. Hence, the possible reactions with Li of the obtained samples here may be according to the

following ones [35, 36]:

The theoretical capacity of $\text{Co}_2(\text{OH})_2\text{CO}_3$ is about 1650 mAh/g if did not consider the contribution of alloying, caculated from the above redox reactions (1-3). Though the alloying of CoLi can not be detected from XRD signals of after discharge/charge cycling samples (Fig. S3), it can be surmised from the lithiation capacity difference between the theoretical value and practical value obtained here.

Life stabilities and rate performance of the samples were also performed here, as shown in Fig. 4c. It can be seen that the sample S without GO suffers from rapid capacity fading, from 1599 mAh g⁻¹ to 780 mAh g⁻¹ during the first 100 cycle at a current density of 1000 mA g⁻¹ after activation at 100 mA g⁻¹ for five cycles. While the S-GO electrode displays considerably improved cycling performance, after 100 cycles, the discharge capacity is still above 1600 mAh g⁻¹ and about 85% was remained at 1000 mA g⁻¹. Furthermore, rate performance of the samples were studied at different current densities stepwise from 100 to 200, 500, 1000, 2000 and 5000 mA g⁻¹, and maintained five cycles for each step (Fig. 4d). The average discharge capacities of the S-GO at 100, 200, 500, 1000, 2000 and 5000 mA g⁻¹ are 2230, 1950, 1770.4, 1629, 1484 and 1242 mAh g⁻¹, respectively. The discharge capacity is still as high as 1242 mAh g⁻¹ at a very high discharge current of 5 A g⁻¹ and about 56% of the capacity was remained when the discharge current increase to be 50 times from 100 mA g⁻¹, indicating a very fast lithiation ability. When the current density was reverted

to 100 mA g^{-1} , the average discharge capacity is still as high as 1801 mAh g^{-1} , only a little lower than the initial value, implying high reversibility and stability of the lithiation reactions. Though the initial capacities of S and S-GO at low discharge current density are comparable, the capacities of S were reduced much more rapidly than those of S-GO and its recover ability is worse. The lithiation ability of the sample S-powder was also presented here, whose initial capacity could also achieve a high value, but underwent a dramatic drop along with cycling and discharge current increase, as shown in Fig 4c and d. The difference in their electrochemical performance could be mainly attributed to the addition of GO, which played an important role in increasing the ratio of nanosheets vs. nanowires and preventing the nanosheets from agglomeration, which would make more nanosheets expose to the electrolyte. Though there is no directly evidence about the distribution of GO, it is believed that GO can improve the electronic conductivity of the electrodes and protect them from broken during the charge/discharge test.

To evaluate the reason of the excellent lithiation performance of the GO composited mixed phase structure of S-GO, morphology and phase structure change of the sample after 100 cycles' test stopped at fully charged state were investigated using SEM and TEM after cleaned with dimethyl carbonate (DMC) and acetone successively. Unexpectedly, the nanosheets still kept their original morphology but much fatter and hence caused a much denser 3D structure, as shown in Fig. 5a. When seen closely, it can be found that some particles were attached on the surface of the fat nanosheets, which are speculated to be CoO_x or some other irreversible products and could stop the neighboring nanosheets to stick together (Fig. 5b). This special structure should be responsible for the good cycling stability as anode, which led to good contact between each other while remained sufficient void space, and hence

benefit the insertion and transportation of Li^+ .

Peeled off from the substrate, amount of loose and irregular nanosheets were detected via a low magnification TEM (Fig. 6a), which is consistent with the SEM analysis. Though the degree of crystallization was dramatically decreased with obvious volume expansion, the sheet shape was kept for S-GO after cycling. SAED pattern (Fig. 6b) exhibits a polycrystalline nature and the diffraction rings can be readily indexed to (310), (414), (703) and (521) crystal planes of the $\text{Co}_2(\text{OH})_2\text{CO}_3$ phase, which is agreed well with the literature reported [30]. Detailed crystal structure can be visualized through HRTEM image in Fig. 6c. It can be seen that the loose nanosheet was composed of small crystal particles with a diameter of several nanometers mingled with some amorphous structure, as seen of the red circles and the red rectangle marked in Fig. 6c. The small crystal particles reveal two sets of lattice fringes with interplane spacing of 0.188 and 0.214 nm, attributed to the (404) and (414) planes of $\text{Co}_2(\text{OH})_2\text{CO}_3$ phase, respectively, which is consistent with the polycrystalline ring described in Fig. 6b. In addition to these small crystal particles, a lot amorphous areas with very poor crystallization are found. Magnified view of one such area marked with a red box in Fig. 6c is presented here as inset. Though there is a little bit distortion, it is not difficult to be seen that the interatomic distances are coincident with that of the carbocyclic ring, indicating the formation of graphite carbon during the charge/discharge test, which may ascribe to the partially irreversible reaction of C^{4+} in CO_3^{2-} to C^0 . The result is in good agreement with the hypothesis we proposed before, the reaction of which was shown in the equations above. Besides, uncontinuous graphene thin layer with a lattice spacing of 0.34 nm can be found on the edge of the sheet (which is further confirmed in Fig. S4), which should originated from the addition of GO during the synthesis process, in accordance with the Raman

result discussed above.

The electrochemical impedance spectroscopy (EIS) technique, so to speak, has been widely used to investigate the charge transfer and Li^+ transport kinetics in various electrode materials. To further evaluate the origin of the excellent lithiation performance of the sample S-GO, EIS technique was employed. As seen in Fig. 7a, both of the plots for sample S and S-GO fresh cells consist of one semicircle in the high frequency region and a sloped straight line in the low frequency region. The diameter of the arc in the high frequency is related to the charge-transfer resistance [37, 38]. An intercept at the Z_{real} (Z') axis at high frequency corresponds to the Ohmic resistance, which represents the electronic resistance of the whole cell, mainly decided by the electrolyte. The inclined line at an approximate 45° angle to the horizontal axis in the lower frequency represents the Warburg impedance, which is inversely proportional to the diffusion coefficient of the lithium ions within the electrode [39]. It can be seen from Fig. 7b that another semicircle appeared in the high frequency range for the sample S-GO after cycling, which should be caused by the inactive layer (SEI film) formed on the surface of the active material during cycling [40]. Corresponding simulated electrochemical parameters of the sample S-GO are obtained and shown in Table 1 using equivalent circuits (Fig. 7c, before cycling; Fig. 7d, after cycling). For the fresh cells before cycling, it is clear that the charge transfer resistance (R_{ct} , 53.96 Ω) and Ohmic resistance (R_{Ω} , 2.10 Ω) of S-GO is smaller than those of the sample S. This behavior can be assigned to an enhanced charge transfer process with the addition of slight GO which improved the electronic conductivity of the sample and induced more contact space for the electrolyte ions among the nanosheets when compared to the relative aggregated nanosheets of S electrode. After cycling, the Ohmic resistance of the sample S-GO (5.94 Ω) got larger, which may be

ascribed to the decomposition of the electrolyte; while the charge-transfer resistance, 57.48 Ω , plus the inactive SEI layer resistance (31.18 Ω), is still comparable with the charge-transfer resistance of the as-assembled cell S though its Warburg impedance was much larger. It can be concluded that the rGO coating layer improved both the Ohmic resistance (R_{Ω}) and charge-transfer resistance (R_{ct}) and retarded the increase of the impedance, thus the capacity was remained during cycling test.

4. Conclusion

In conclusion, rGO coated mixture of $\text{Co}_2(\text{OH})_2\text{CO}_3$ nanosheet arrays and a few CoO nanowires were synthesized and deposited on copper foil directly via a simple one-step hydrothermal procedure. Benefited from its unique chemical composition, spatial structure and the direct contact with current collector, the obtained sample exhibited high performance as anode material for Li ion batteries, which delivered a very high reversible capacity of 2,100 mAh g^{-1} at 100 mA g^{-1} , a high rate of lithiation ability (still as high as 1,240 mAh g^{-1} at 5,000 mA g^{-1}), and a high cycling stability (the capacity of 1600 mAh g^{-1} was remained from 1900 mAh g^{-1} after 100 cycles' test at 1,000 mAh g^{-1}). HRTEM analysis indicates that CO_3^{2-} was involved into the energy storage process, which should be the key factor of such high capacity; while the covered layer of rGO was suspected to contribute to the high stability, which protected the nanosheets to be broken or reunited. Additional, the intrinsic properties of different phase structure also play important roles on the structure retention, seen from the different shape change of $\text{Co}_2(\text{OH})_2\text{CO}_3$ and CoO at the same condition. It can be said that carbonate based compounds are very promising alternatives as anode materials. And further work focusing on the energy storage behavior and structure design need to be done in the future study to realize the commercial use of carbonate based compounds.

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Table captions

Table.1. Ohmic resistance (R_{Ω}), charge-transfer resistance (R_{ct}) and inactive layer resistance (R_f) for the samples.

Figure captions

Fig. 1.

(a) SEM images, (b) TEM image (stripped off from the substrate) and (c) cross-section image of the “S-GO” sample before test; (d) SEM image of the sample “S” before test.

Fig. 2.

(a) Schematic illustration of the growth of cobalt hybrid oxides arrays on Cu foil; (b) XRD patterns and (c) Raman spectra of the as-prepared samples “S-GO” and “S”.

Fig. 3.

TEM/HRTEM images of the as-prepared sample “S-GO”: (a, d) Low magnification TEM images; (b, e) HRTEM images, showing the locally enlarged corresponding TEM images indicated by the red boxes in the left; (c, f) Fast Fourier Transform (FFT) patterns, corresponding to the HRTEM images, respectively. The images a, b and c revealed the information of a nanosheet, while d, e and f exhibited the information of a nanowire.

Fig. 4.

Discharge/charge profiles of (a) “S” and (b) “S-GO” at a current density of 100 mA g^{-1} ; (c) Cycling performance of the samples in a voltage range of 0.01-3.0 V vs. Li/Li^+ at 1000 mA g^{-1} ; (d) Rate performance of the electrodes at different current densities.

Fig. 5.

SEM images at (a) low and (b) high magnification of the “S-GO” sample after 100 cycles and cleaned with DMC and acetone successively.

Fig. 6.

TEM/HRTEM images of one nanosheet from the after cycling test sample of “S-GO”: (a) low magnification TEM image, (b) SAED pattern and (c) HRTEM image. The fringe spacing from a lot small grains of 0.188 nm and 0.214 nm correspond to the separation between the (404) and (414) lattice planes of $\text{Co}_2(\text{OH})_2\text{CO}_3$, respectively. Amorphous carbon areas can be observed and are mingled with these small grains, while on the edge very thin rGO layer is looming.

Fig. 7.

Nyquist plots: (a) fresh cell of the “S” and “S-GO”, (b) “S-GO” before and after cycling. (c, d) the corresponding equivalent circuits used to fit the experimental data, (c) before and (d) after cycling samples.

Table .1.

Sample	S (before)	S-GO (before)	S-GO (after)
R_{Ω}/Ω	2.71	2.10	5.94
R_f/Ω			31.18
R_{ct}/Ω	89.21	53.96	57.48

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6.

Fig. 7