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Nickel–cobalt oxides/carbon nanoflakes as anode materials for lithium-ion batteries

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ABSTRACT

Novel nickel–cobalt oxides/carbon nanoflakes with Ni/Co molar ratio = 1:1 and 1:2 have been synthesized by a convenient hydrothermal method followed by a simple calcination process. X-ray diffraction results showed that the composites were composed of NiO, Co_3O_4, and carbon. Scanning electron microscope measurements demonstrated that the composites were flakes less than 100 nm in thickness, and the corresponding energy dispersive spectroscopy mapping showed that the carbon was distributed homogeneously in the composites. The electrochemical results showed that the composite electrodes exhibited low initial coulombic efficiency and excellent charge–discharge cycling stability. Additionally, the effect of different Ni/Co molar ratios on the electrochemical properties of the composites was investigated, and better performance was obtained for the sample with a Ni/Co molar ratio of 1:2.

1. Introduction

A worldwide effort has been made to search for materials with larger capacities and better cycling performances in order to find a better replacement for conventional graphite anode for lithium-ion batteries [1,2]. It was found that transition-metal oxides (MO, where M is Co, Ni, Cu, or Fe) can provide a large reversible capacity (700 mAh/g), good cycling performance and high recharging rates [3]. The reaction mechanism of these metal oxides with lithium involves the reversible reduction and oxidation of metal (M) nanosized particles dispersed into a lithia matrix (Li_2O), followed by the formation/decomposition of a solid electrolyte interface (SEI). Although the average lithium removal voltage for transition-metal oxides was above 1.0 V *vs.* Li, the Li-ion cells using them as anode still can deliver 100% of their capacity at voltages >1.2 V, a voltage anticipated to be the cut-off discharge voltage of tomorrow's electronics [4]. However, it has been found that the electrochemical properties of the electrodes are restricted by the large volume change, the serious aggregation or pulverization of the active particles during charge–discharge, and the poor conductivity of the transition metal oxides [5].

Recently, binary Ni–Co oxides have been developed as alternative electrode materials for supercapacitors, and their electrochemical properties in terms of oxygen evolution reaction (OER) have also been studied widely in an alkaline medium [6]. Synergistic electrocatalytic behaviour has been found and depends on the composition of the oxides [7]. Moreover, it has also been found that the composition of binary Ni–Co oxides has effects on

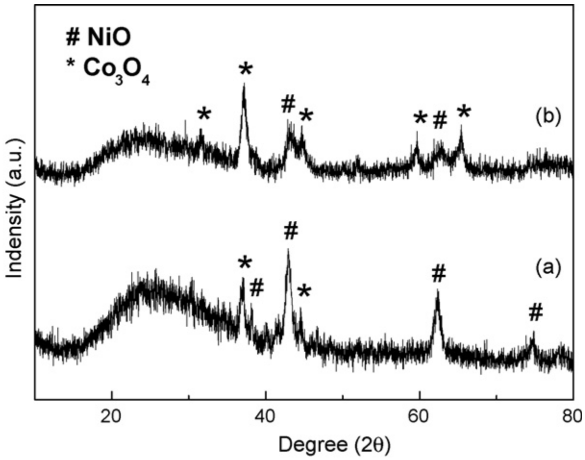

Fig. 1. XRD patterns of as-prepared nickel–cobalt oxide/C powders for Ni/Co molar ratio = (a) 1:1 and (b) 1:2.

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their capacitive properties [8]. However, few scientists have investigated the electrochemical properties of binary Ni–Co oxides as anode materials for lithium-ion batteries and the effects of the composition of the oxides on the properties.

It has been reported that the preparation methods for binary Ni–Co oxides include thermal decomposition [9,10], solution deposition [11], combinatorial sputtering deposition [12], single-target sputter deposition [12], hydroxide co-precipitation [13], and so on. Binary Ni–Co oxides/carbon nanotube (CNT) composite electrodes were also prepared by the electrodeposition method [14]. However, it was difficult to accurately control the composition of the binary oxides.

It is well known that the hydrothermal method is an idea technique for processing very fine powders having high purity, controlled stoichiometry, narrow particle size distribution, high crystallinity, controlled morphology, etc. [15]. In the work reported here, we describe an easy route to isochronously synthesize nickel–cobalt oxides/C nanoflakes via a low-temperature hydrothermal method followed by calcination. Poly(ethylene glycol), a typical non-toxic, non-immunogenic, non-antigenic, and protein-resistant polymer reagent with long polymer chains, was employed as the carbon source. Carbon in the composite provides a good conductive matrix, which not only maintains the integrity of the electrode, but also decreases the polarization, thus enhancing capacity retention. It was found that the composition of binary oxides in the composites was controlled easily and accurately, and the effect of different Ni/Co molar ratios on their electrochemical properties as anode materials for lithium-ion batteries was further investigated.

2. Experimental

2.1. Preparation of nickel–cobalt oxide/carbon nanoflakes

All the chemical reagents were analytically pure and used without further purification. In a typical experimental procedure,

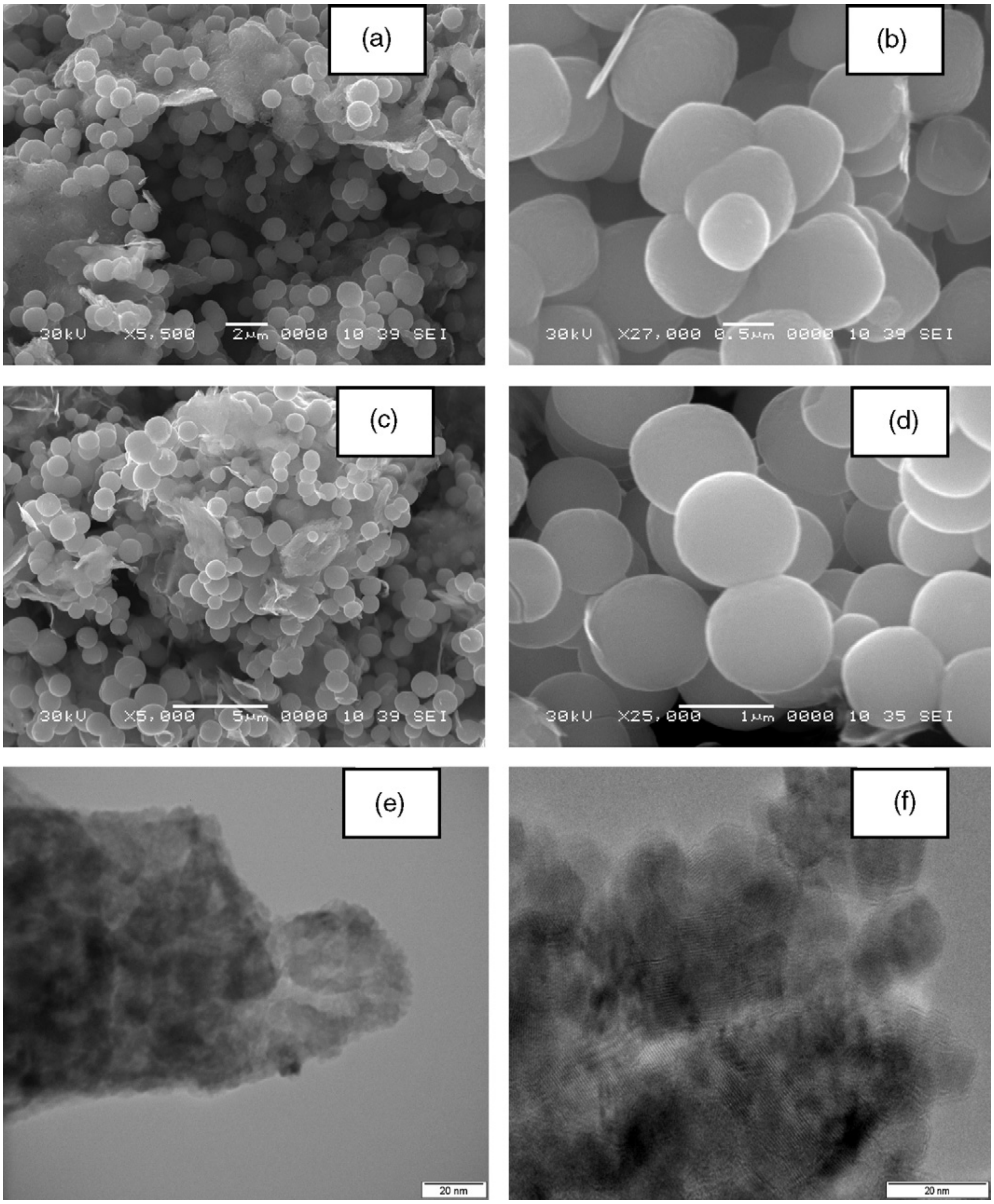

Fig. 2. SEM images of as-prepared nickel–cobalt oxide/C nanoflakes for Ni/Co molar ratio = (a), (b) 1:1 and (c), (d) 1:2 at different magnifications. TEM images of as-prepared nickel–cobalt oxide/C nanoflakes for Ni/Co molar ratio = (e) 1:1 and (f) 1:2.

1 M $Ni(NO_3)_2$ (Aldrich) and 1 M $Co(NO_3)_2$ (Aldrich) (with the Ni/Co molar ratio 1:1 and 1:2, respectively) were added dropwise to equivalent molar number 1 M PEG-600 (Aldrich) methanol solution under continuous stirring at room temperature to obtain a homogeneous precursor solution. A stoichiometric proportion of the precursor and NaOH (4 M) were added under stirring to a 125-mL Teflon-lined autoclave, which was filled to one-fourth by volume. Then, the autoclave was sealed and heated to 160 °C for 24 h. After the reaction, the autoclave was cooled down naturally. The resulting products were washed with ethanol and distilled water to ensure total removal of the inorganic ions, and then dried under vacuum at 80 °C for 4 h as the intermediate product. After that, the intermediate product was calcined at 300 °C for 2 h in argon.

2.2. Sample characterizations

X-ray powder diffraction (XRD) analysis was conducted using a Philips 1730 X-ray diffractometer with Cu Kα radiation (λ = 1.54056 Å). Scanning electron microscopy (SEM) was performed using a JEOL JSM 6460A instrument with JEOL energy dispersive spectroscopy (EDS) and EDS-X-ray mapping systems. A JEOL 2011 200 keV transmission electron microscope (TEM) was further employed to examine the morphology of the products.

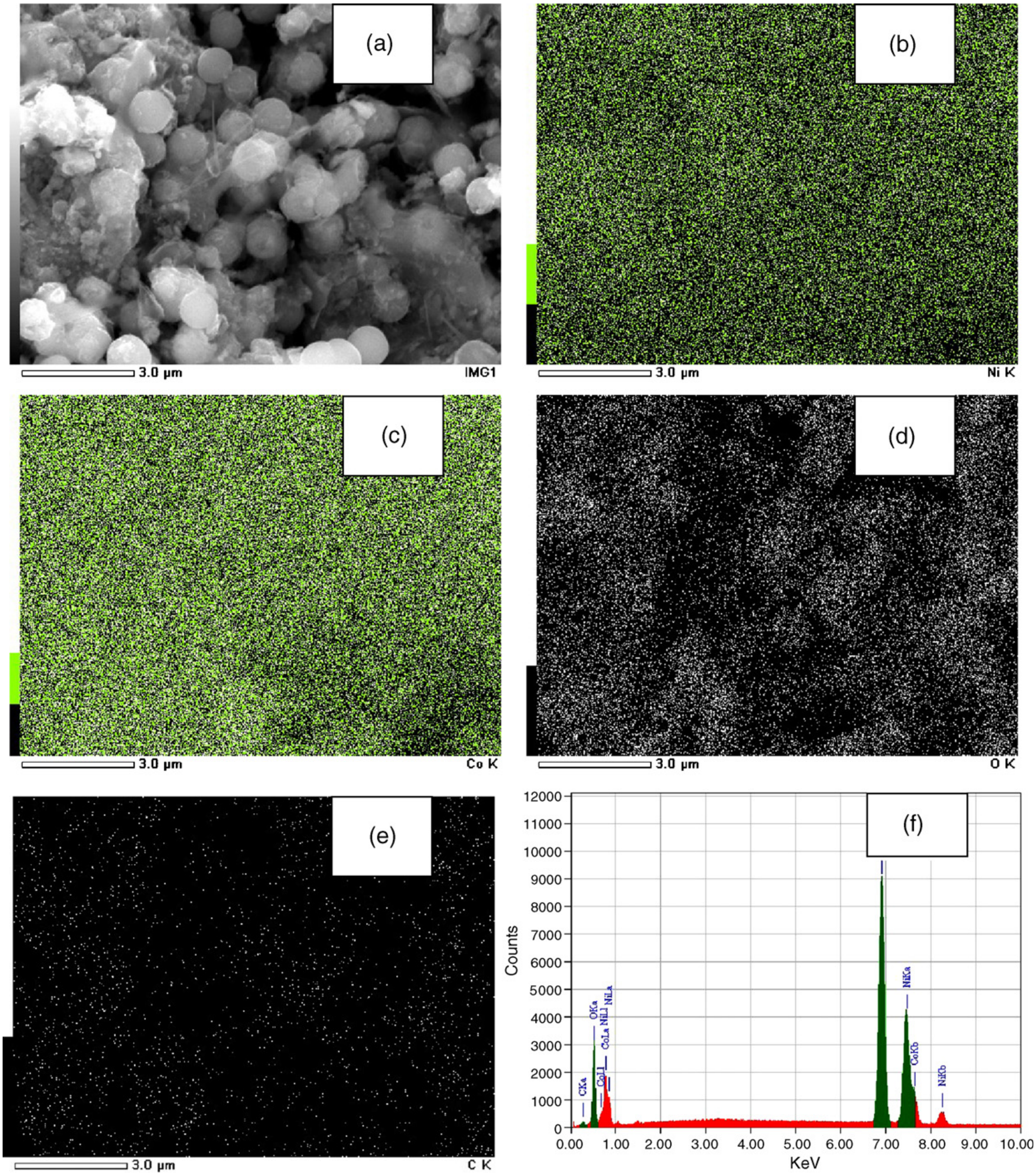

Fig. 3. A SEM image of as-prepared nickel–cobalt oxide/C nanoflake for Ni/Co molar ratio = 1:1 (a) and the corresponding EDS mapping for the elements Ni (b), Co (c), O (d) C (e) and the EDS spectrum (f).

A typical slurry was obtained by grinding a mixture of active material, carbon black, and poly(vinylidene fluoride) (PVDF) dissolved in *N*-methyl-2-pyrrolidinone (NMP) with a weight ratio of 70:15:15. It was then pasted onto a copper foil (1 cm^2) to form the electrode. After the electrode was dried at 100 °C for 4 h under vacuum, it was compressed and then weighed. The electrochemical behaviour of the materials was examined via CR2025 coin-type cells with lithium metal as the counter electrode, Celgard 2400 membrane as the separator, and 1 M $LiPF_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume) as the electrolyte. The cells were assembled in an argon-filled glove box (Mbraun, Unilab, Germany). The charge–discharge measurements were conducted at ambient temperature on a multi-channel battery cycler in the voltage range between 0.01 V and 3.0 V at a current density of 40 mA/g. Cyclic voltammetry (CV) measurements were performed using a CHI instrument at a scanning rate of 1 mV/s.

3. Results and discussion

Fig. 1(a) and (b) shows the X-ray diffraction patterns of the as-synthesized powders for Ni/Co molar ratio = 1:1 and 1:2, respectively. The diffraction peaks at 31.27°, 36.26°, 44.19° and 65.23° can be indexed as the (2 2 0), (3 1 1), (4 0 0), and (4 4 0) crystal planes of Co_3O_4 (JCPDS No. 09-0418), respectively. Peaks at 37.40°, 43.50°, 63.00° and 75.40° corresponds to the (1 1 1), (2 0 0), (2 2 0), and (3 1 1) crystal planes of NiO (JCPDS No. 04-0835). The broad diffraction peak at about 24° is related to the carbon. The results indicate the products are composites composed of carbon and nickel–cobalt oxides, with more NiO present for a Ni/Co molar ratio of 1:1 and more Co_3O_4 for a Ni/Co molar ratio of 1:2.

Fig. 2(a)–(d) show SEM images of the as-prepared samples at different magnifications for Ni/Co molar ratio = 1:1 and 1:2, respectively. It can be seen that there are no obvious differences between the two samples. The low-magnification views demonstrate that the samples are composed of flakes embedded in a thin silk-like material, and the flakes shown in the higher magnification images are uniform, with an average diameter of about 0.5 μm and a thickness of less than 100 nm. Fig. 2(e) and (f) further shows TEM images of as-prepared samples for Ni/Co molar ratio = 1:1 and 1:2, respectively. It can be seen that fine particles, which appear dark, are distributed in a brighter matrix. Based on EDS analysis, it was found that the fine particles are the oxides, while the brighter matrix is carbon. Further high-resolution imaging is required to fully characterize the distribution of carbon within the oxide particles.

However, SEM-EDS analysis indicated a uniform carbon concentration, as shown in Fig. 3. Fig. 3(a) is a SEM image of the sample with a Ni/Co molar ratio of 1:1, and Fig. 3(b)–(e) shows the corresponding EDS mappings for the elements of Ni, Co, O, and C, respectively. The bright spots correspond to the presence of each element. It is obvious that the distribution of carbon in the composite is homogeneous. It is reasonable to believe that the oxides and carbon particles were thoroughly amalgamated. The representative EDS analysis (Fig. 3(f)) indicates that the Ni/Co ratio in the composite is 0.97, near the ratio of the reaction reagents, while the carbon content is 11.56 mol%. The same measurement was also conducted for the sample with the Ni/Co molar ratio of 1:2, and the results show that the Ni/Co ratio in the composite is 0.51 and the carbon content is as high as 20.10 mol%.

Fig. 4 shows the cyclic voltammetric curves of the nickel–cobalt oxide/C nanoflake electrodes for a Ni/Co molar ratio of 1:1. A reduction peak at about 0.2 V in the first cycle corresponds to the decomposition of the oxides into Ni and Co, and the formation of amorphous Li_2O and the SEI. The two oxidation peaks located at about 1.6 V and 2.4 V can be attributed to the reverse process where metals are reoxidized to oxides and Li_2O decomposes. In the subsequent cycle, the reduction peak becomes broad and shifts up to around 0.8 V, while the oxidation peaks remain at the same potential with a slow decrease in peak intensity.

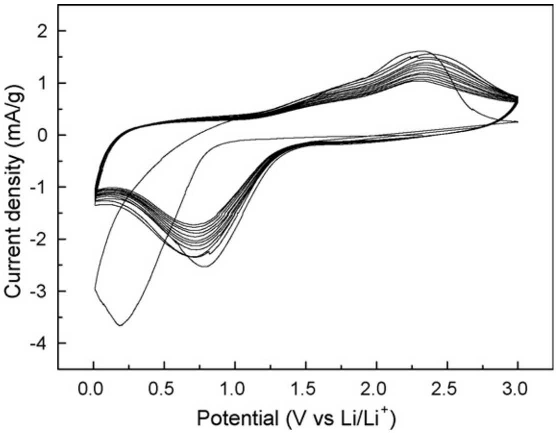

Fig. 4. Cyclic voltammograms of the electrode made from nickel–cobalt oxide/C nanoflake for Ni/Co molar ratio = 1:1.

Fig. 5(a) and (b) shows the charge/discharge curves of nickel–cobalt oxide/C nanoflake electrodes for Ni/Co molar ratios of 1:1 and 1:2, respectively. For both samples, the potential rapidly falls and reaches a long voltage plateau at around 0.85 V in the first discharge process, followed by a gradual decrease to 0.01 V, 798.5 mAh/g and 1058.2 mAh/g initial discharge capacity was obtained, respectively. The first charge process exhibits a higher and more sloping voltage profile, with two inconspicuous plateaus

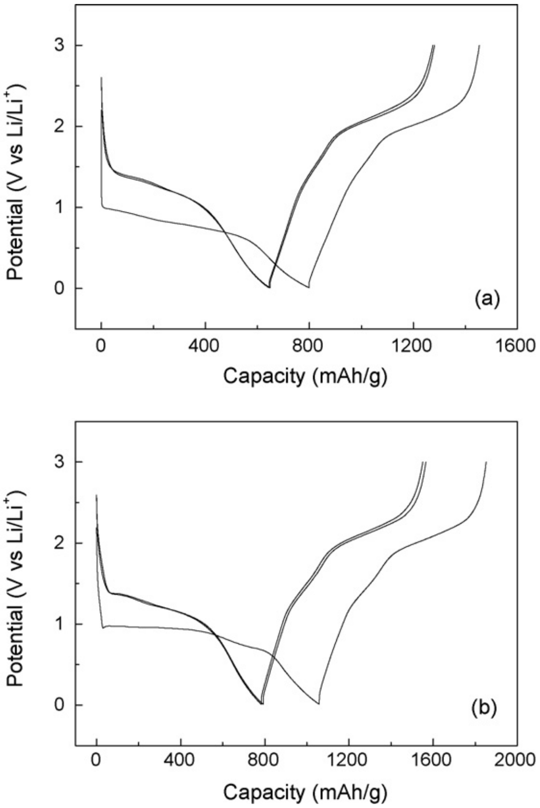

Fig. 5. Charge–discharge curves for the first three cycles of the electrodes made from nickel–cobalt oxide/C nanoflakes for Ni/Co molar ratio = (a) 1:1 and (b) 1:2.

Table 1
Comparison of the electrochemical properties of nickel–cobalt oxide/carbon nanoflakes with Ni/Co molar ratio = 1:1 and 1:2 that were fabricated in this work with those of NiO and Co_3O_4 with different shapes reported in the literatures

Samples	Current density	Potential range (V *vs.* Li/Li^+)	Initial capacity (mAh/g)	Initial coulombic efficiency (%)	Capacity retention	Reference
Nickel–cobalt oxides/carbon nanoflakes with Ni/Co molar ratio = 1:1	40 mA/g	3.0–0.01	798.5	82.1	555.8 mAh/g after 30 cycles	This work
Nickel–cobalt oxides/carbon nanoflakes with Ni/Co molar ratio = 1:2			1058.2	75.0	699.4 mAh/g after 30 cycles	
Nanosized NiO	14.36 mA/g	3.0–0.01	About 1000	About 65	About 400 mAh/g after 30 cycles	[3]
NiO nanopowder	100 mA/g	3.0–0.02	997.4	64.9	About 500 mAh/g after 30 cycles	[16]
NiO nanotube	25 mA/g	3.0–0.01	About 610	Low	200 mAh/g after 20 cycles	[17]
Spherical NiO nanoshaft	50 mA/g	3.0–0.01	1300	–	410 mAh/g after 30 cycles	[18]
Nanosized Co_3O_4	C/5	3.0–0.01	1411	34	913 mAh/g after 20 cycles	[19]
Nanosize Co_3O_4 powders	20 mA/g	3.0–0.01	780	–	About 460 mAh/g after 30 cycles	[20]
Nanosized Co_3O_4	0.1C	3.0–0.01	1380	67	550 mAh/g after 10 cycles	[21]
Co_3O_4 microspheres	50 mA/g	3.0–0.01	–	–	550 mAh/g after 25 cycles	[22]

and lower capacities of 655.2 mAh/g for a Ni/Co molar ratio of 1:1 and 793.5 mAh/g for a Ni/Co molar ratio of 1:2. It can be calculated that the initial coulombic efficiency is 82.1% and 75.0%, respectively. In the second discharge process, the voltage plateau appears at a higher voltage of about 1.3 V, while the amplitude of the plateau is reduced. A reversible capacity of 648.8 mAh/g and 792.5 mAh/g can be achieved, respectively. There are no obvious differences in subsequent cycles.

Fig. 6 presents the cycling behaviour of the nickel–cobalt oxide/C nanoflake electrodes for Ni/Co molar ratio = 1:1 and 1:2, respectively. It can be seen that higher capacity and better cyclic retention are obtained for the higher amount of Co_3O_4. The capacity after 30 cycles is maintained at 555.8 mAh/g and 699.4 mAh/g, which is about 85.7% and 88.3% of the reversible capacity, respectively. There is no serious capacity fading, especially for the sample with the higher amount of Co_3O_4, suggesting that no observable structural degradation of the nanoflakes takes place during repeated cycling. For comparison purposes, the electrochemical properties of nickel–cobalt oxide/carbon nanoflakes with Ni/Co molar ratio = 1:1 and 1:2 that were fabricated in this work and those of NiO and Co_3O_4 materials reported in the literatures are summarized in Table 1. Although the composite electrodes prepared in this work have slightly lower initial capacity compared with some pure NiO or Co_3O_4 samples, the initial coulombic efficiencies are higher than those of the individual oxides, and the capacity retention is better than that of NiO. As mentioned above, transition-metal oxides show poor conductivity, and the electrodes suffer large volume change, with serious aggregation or pulverization of active particles during charge–discharge. It has been proposed that mixed transition metal oxide can react reversibly with a larger amount of lithium [23] and exhibits improved electrode performance compared to pure oxides, as a consequence of the synergistic effects of both transition metal elements [24]. In this work, carbon further provides a good conductive matrix, which not only maintains the integrity of the electrodes, but also decreases the polarization, thus enhancing the capacity retention. Moreover, the good interface affinity between the oxides and the carbon particles ensures structural stability during cycling and results in the excellent electrochemical performance of the composites. The higher amounts of Co_3O_4 and carbon lie behind the better electrochemical performance for the composite with a Ni/Co molar ratio of 1:2.

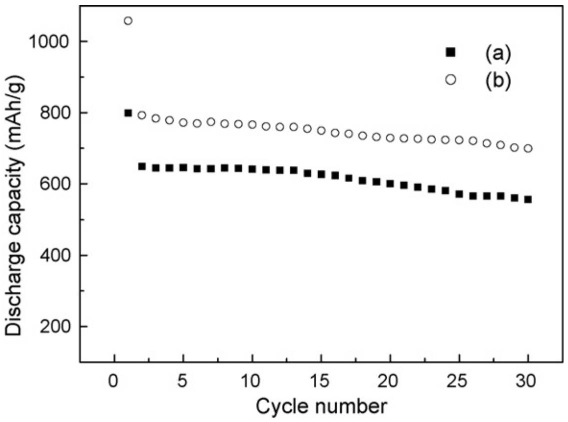

Fig. 6. Discharge capacity *vs.* cycle number curves of the electrodes made from nickel–cobalt oxide/C nanoflakes for Ni/Co molar ratio = (a) 1:1 and (b) 1:2.

4. Conclusions

Nickel–cobalt oxide/C nanoflakes for Ni/Co molar ratio = 1:1 and 1:2 were successfully prepared by the hydrothermal method, followed by calcination in argon at 300 °C for 2 h. At a current density of 40 mA/g, 648.8 mAh/g and 792.5 mAh/g reversible capacity can be obtained, and the capacity retention was 85.7% and 88.3% after 30 cycles, respectively. It is notable that the initial coulombic efficiency reached as high as 82.1% and 75.0%, respectively. The excellent electrochemical performance of the nanoflakes could be mainly attributed to the high distribution of oxide particles within the carbon matrix and the good interface affinity between oxide and carbon particles, which resulted from the *in situ* preparation of the oxides and carbon. The higher amounts of Co_3O_4 and carbon lie behind the better electrochemical performance for the composite with a Ni/Co molar ratio of 1:2.

Acknowledgement

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