Chemical reduction-induced oxygen deficiency in Co3O4 nanocubes as advanced anodes for lithium ion batteries

Liu, Yanguo; Wan, Haicheng; Jiang, Nan; Zhang, Wanxing; Zhang, Hongzhi; Chang, Bingdong; Wang, Qing; Zhang, Yahui; Wang, Zhiyuan; Luo, Shaohua

Total number of authors: 11

Published in: Solid State Ionics

Link to article, DOI: 10.1016/j.ssi.2019.02.014

Publication date: 2019

Document Version
Peer reviewed version

Citation (APA):

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.
Chemical Reduction-Induced Oxygen Deficiency in Co₃O₄ Nanocubes as Advanced Anodes for Lithium Ion Batteries

Yanguo Liu,ᵃᵇᶜ,¹,* Haicheng Wan,ᵃ¹ Nan Jiang,ᵇ Wanxing Zhang,ᵇ Hongzhi Zhang,ᵇ Bingdong Chang,ᵈ Qing Wang,ᵃᵇᶜ Yahui Zhang,ᵃᵇᶜ Zhiyuan Wang,ᵃᵇᶜ Shaohua Luo,ᵃᵇᶜ Hongyu Sunᵈ,e,*

ᵃ School of Materials Science and Engineering, Northeastern University, Shenyang 110004, PR China
ᵇ School of Resources and Materials, Northeastern University at Qinhuangdao, Qinhuangdao 066004, PR China
ᶜ Key Laboratory of Dielectric and Electrolyte Functional Material Hebei Province, Qinhuangdao 066004, PR China
ᵈ National Centre for Nano Fabrication and Characterization, Technical University of Denmark, Kongens Lyngby 2800, Denmark
ᵉ Department of Micro- and Nanotechnology, Technical University of Denmark, Kongens Lyngby 2800, Denmark

¹ The authors contribute equally to this work.
* Corresponding authors.
E-mail addresses: lyg@neuq.edu.cn (Y. Liu), hsun@nanotech.dtu.dk (H. Sun).
ABSTRACT

Cobalt (II, III) oxide (Co$_3$O$_4$) nanostructures have attracted much attention as a candidate for anode materials in lithium-ion batteries (LIBs) due to its unique physical/chemical properties and high specific capacity. However, critical issues, such as low electronic conductivity, inefficient ionic diffusion, and large volume change during battery operation, have to be addressed before practical applications. In this work, we report a facile chemical reduction approach to modify Co$_3$O$_4$ nanocubes by NaBH$_4$ solution treatment. The microstructure and chemical composition analysis indicate that the modified Co$_3$O$_4$ nanocubes are oxygen deficient and other secondary phases are not formed during the processing. The degree of oxygen deficiency can be well controlled by altering the concentration of NaBH$_4$ solution. When evaluated as the anodes for LIBs, the optimized sample shows a reversible capacity of 873.5 mAhg$^{-1}$ after 50 cycles at a current density of 0.1 Ag$^{-1}$, and a charge-discharge capacity of 569.1 mAhg$^{-1}$ at a higher current density of 5 Ag$^{-1}$. The balanced oxygen deficiency and crystallinity in the chemically reduced nanostructured electrodes are supposed to be responsible for the improved lithium storage properties. We believe that the facile solution-based chemical reduction strategy provides an alternative way to control the defects in different functional nanostructures for broader applications.

**Keywords**: Oxygen deficiency; Chemical reduction; Co$_3$O$_4$ nanocubes; Anode materials; Lithium-ion batteries.
1. **Introduction**

Developing efficient and durable energy storage systems for renewable energy resources is a promising approach to constrain the depletion of fossil fuels and alleviate serious environmental issues [1-5]. Among various electrochemical energy storage devices, rechargeable lithium-ion batteries (LIBs) have been successfully applied in modern society due to the advantages of high energy density, low self-discharge rate, and no memory effect, making it favorable for applications such as mobile electronics, hybrid electric vehicles, and large-scale electric energy storage [6, 7]. To optimize and improve the performance of LIBs (mostly characterized by energy density, rate capability, lifetime, and safety), it becomes essential to develop the key components in battery system, especially the electrode materials. Typically, the commercial LIBs employ graphite as anode material, nevertheless, it cannot fulfill the increasing requirements for high performance LIBs, limited by the low theoretical capacity of 372 mAhg\(^{-1}\) and serious safety problems arising from low Li ion intercalation potential [8-10]. In this regard, many transition metal oxides (TMOs, such as the oxides of iron, cobalt, nickel, copper, etc) have been studied as alternative anode materials due to their high theoretical capacities (600 ~ 1200 mAhg\(^{-1}\)), multiple chemical valence states, higher operating voltages than graphite, large natural abundance and low manufacture cost [11-17].

Among different TMOs, cobalt (II, III) oxide (Co\(_3\)O\(_4\)) with a theoretical capacity of 890 mAhg\(^{-1}\) is considered as one of the most promising electrodes for LIBs [18, 19].

In addition, Co\(_3\)O\(_4\) materials also show excellent anti-corrosion property and
availability. However, the practical usages of $\text{Co}_3\text{O}_4$ anodes is hindered by the low electronic conductivity and large volume change during charging and discharging operations, causing sluggish electron transport kinetics, serious particle agglomeration, electrochemical pulverization, unstable solid-electrolyte interphase (SEI) formation and loss of contact with current collectors [20]. To overcome these disadvantages, the following two main strategies have been developed: (1) design and synthesis of $\text{Co}_3\text{O}_4$ nanostructures, e.g. nanowires, nanosheets, three dimensional micro/nano hierarchical architectures [21-25]. These nanostructures can accommodate the volume change during battery cycling, reduce the ion/electron diffusion distance and provide more active sites for ion storage, which are favorable to increase the cycling rates and the energy density; (2) integration the active materials with conductive agents (carbon nanotubes, graphene, conducting polymers, etc). The addictives have been demonstrated to enhance electron conductivity and chemically modify the interface between electrode and electrolyte [26-30]. It should be mentioned that the addition of conductive agents unavoidably decreases the effective volume density of active materials.

Recently, engineering surface defect in TMO nanostructures, such as oxygen deficiency and heterointerface, has been employed to study their effects on electrochemical performance of electrode materials [29-31]. The nanoscale defects can promote the charge transport kinetics and retain the integrity of the electrode structure, thus enhancing the electrochemical activity [29, 30]. In our previous works, different methods have been developed, for example, laser irradiation treatment [34],
gas phase annealing [35], and solution phase reduction [36], to modify the defect chemistry and interfacial structure in Co$_3$O$_4$ anodes. The results suggest that the oxygen vacancies and surface CoO layer are simultaneously formed in the modified Co$_3$O$_4$ nanostructure, leading to an improved electrochemical performance. To facilitate the design and synthesis of high performance electrodes, it is crucial to understand and distinguish the roles of oxygen vacancies and interfacial structures in the performance enhancement.

In this work, we studied the modification of Co$_3$O$_4$ nanocubes by chemical reduction with NaBH$_4$ solution. By tuning the concentration of NaBH$_4$ solution, oxygen vacancies and their amount can be controlled, and no other phase was formed during the reduction process. Electrochemical measurement results show that the optimized sample possesses a reversible capacity of 873.5 mAhg$^{-1}$ after 50 cycles at a current density of 0.1 Ag$^{-1}$, and a charge-discharge capacity of 569.1 mAhg$^{-1}$ at a higher current density of 5 Ag$^{-1}$. The improved lithium storage properties are attributed to the balanced oxygen deficiency and crystallinity in the chemically reduced nanostructured electrodes.

2. Experimental

2.1. Materials synthesis and NaBH$_4$ solution treatment

The Co$_3$O$_4$ nanocubes were synthesized by a one-step hydrothermal method. In a typical process, cobalt(II) nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O, 0.04 mol) and sodium hydroxide (NaOH, 0.01 mol) were dissolved in deionized water (40 mL). The mixture
was stirred to form a homogeneous solution, which was transferred into a Teflon-lined stainless steel autoclave for reaction at 180 °C for 5 h. After cooling naturally to room temperature, the product was washed three times with deionized water and anhydrous ethanol, and dried in an oven at 60 °C for 12 h. The as-prepared sample is named as Co₃O₄-AP.

For NaBH₄ solution treatment, the Co₃O₄-AP sample (0.5 g) were placed in freshly prepared, ice-cold NaBH₄ solution (100 mL) with different concentrations (5 mM, 10 mM, 100 mM, and 1 M). The mixture was continuously stirred by a glass rod during the reaction (30 min). After that, the precipitate was collected by centrifugation and washed successively with deionized water and anhydrous ethanol for several times. Finally the products were dried in an oven at 60 °C for 12 h. The treated samples are named as Co₃O₄-s (s=5 mM, 10 mM, 100 mM, and 1 M).

2.2. Materials characterization

X-ray diffraction (XRD, DX-2500) with Cu-Kα irradiation (λ=1.5418 Å) was used to analyze the crystallographic information and phase composition of the samples. Field-emission scanning electron microscope (FESEM, ZEISS SUPRA 55, 5 keV) and transmission electron microscope (TEM, JEOL 2100 Plus, 200 keV) were employed to examine the morphology. The surface composition and valence-state were characterized by X-ray photoelectron spectroscopy (XPS, Thermo Fisher 250XI).

2.3. Electrochemical measurements

The lithium storage performance was evaluated by using coin cell configuration
and measured by LAND CT2001A apparatus. The working electrodes were constructed by blending the active materials, acetylene black, and polyvinylidene fluoride (PVDF) with a weight ratio of 8:1:1. After stirred the mixture for 3 h, the slurry was coated onto a Cu foil (which was used as a current collector), and dried in a vacuum oven at 60 °C for 8 h. Then the electrodes were cut into disks (12 mm in diameter) and dried at 120 °C for 8 h in vacuum. Lithium foil and Celgard 2400 were used as the counter/reference electrode and the separator, respectively. The electrolyte was prepared by dissolving LiPF₆ (1 M) in a mixed solution of ethylene carbonate/dimethyl carbonate (EC/DMC, weight ratio 1:1). All the cells were aged for 12 h before further electrochemical tests. The charge-discharge profiles and cyclic stability were measured at a current density of 0.1 Ag⁻¹ with the potential window of 0.01 - 3 V (vs. Li⁺/Li). The rate capability was evaluated at different current densities (0.1, 0.5, 1, 5, and 0.1 Ag⁻¹). Electrochemical workstation (CHI 1000C, Chenhua Instrument, Shanghai) was used to performed the cyclic voltammetry (CV) measurements. CV curves were recorded between 0.01 V and 3 V (vs. Li⁺/Li) at a scan rate of 0.5 mVs⁻¹. Electrochemical impedance analyzer (Solartron 1260 + 1287) was used to analyze the electrochemical impedance spectroscopy (EIS), which was carried out at open circuit potential (OCP) with a frequency ranging from 1 mHz to 100 kHz at an amplification voltage of 10 mV. All the measurements were carried out at room temperature.

3. Results and discussion
The initial cube-like Co$_3$O$_4$-AP particles were synthesized by a simple one-step hydrothermal reaction. In chemical reduction process, the Co$_3$O$_4$-AP sample was subjected to react with freshly prepared NaBH$_4$ solution with different concentrations. XRD analysis is performed to characterize the phase purity of the samples both before and after the solution phase treatment (Fig. 1). Diffraction peaks of all the samples match well with the standard pattern of spinel Co$_3$O$_4$ phase (JCPDS No. 74-2120). No other peaks from possible impurity phases can be detected even after the chemical reduction treatment in NaBH$_4$ solution. We also found that the diffraction peaks of the treated samples, especially Co$_3$O$_4$-1 M sample, are not as sharp as that of the pristine Co$_3$O$_4$, indicating a reduced crystallinity after soaking in the NaBH$_4$ solutions. The reduced crystallinity is supposed to be caused by following reasons: (1) oxygen atoms in Co$_3$O$_4$ lattice are removed during the NaBH$_4$ solution treatment, which can undermine the ordered crystal structures; (2) the solution reaction was performed at room temperature, thus possible structural reorganization is not kinetically favored; (3) during modification, the formation and collapse of hydrogen bubbles might induce powerful waves of vibration applying on the particle surface, further affecting the surface lattice [36].
Fig. 1. XRD patterns of Co$_3$O$_4$-AP, Co$_3$O$_4$-5 mM, Co$_3$O$_4$-10 mM, Co$_3$O$_4$-100 mM, and Co$_3$O$_4$-1 M samples. All diffraction peaks match well with the standard diffraction of spinel Co$_3$O$_4$ phase (JCPDS No. 74-2120).

Fig. 2 displays the typical FESEM images with low- and high-magnification, and size distributions of different Co$_3$O$_4$ samples. The initial Co$_3$O$_4$-AP sample shows a typical cubic morphology with smooth surfaces. The average particle size is ~210 nm (Fig. 2a-c). After the reaction with NaBH$_4$ solutions (5 mM – 1 M), the Co$_3$O$_4$ samples preserve the cubic facet morphology with approximate the same particle size (210 – 230 nm). The slight average size change is considered to be caused by reactions with NaBH$_4$ solutions. The roughness of nanocube surface increase gradually with an increasing NaBH$_4$ concentration. At higher concentrations (100 mM and 1 M, Fig. 2k, n), some ultrathin nanosheets are formed and attached on the
surface of nanocubes. The detailed microstructure characterization results by TEM observing are illustrated in Fig. 3. Low-magnification TEM images indicate that the both as-prepared and treated samples consist of uniform nanocubes. The Co$_3$O$_4$-AP nanocubes possess clean and smooth surfaces, while a higher roughness can be observed on the surface of treated nanocubes. In Co$_3$O$_4$-100 mM and Co$_3$O$_4$-1 M samples, thin sheets can be clearly seen on the surface of the cubes, which are in good agreement with the FESEM studies. Selected area electron diffraction patterns (insets) show that each cube in the samples is single crystalline with \{001\} planes as the exposed facets. High resolution TEM (HRTEM) images acquired from the edge area of an individual cube show clear lattice fringes crossing from the inner region to surfaces, and the spacing values of ~0.293 and ~0.210 nm correspond to the (220) and (400) planes of spinel Co$_3$O$_4$ phase. In addition, no obvious surface layer with secondary crystalline structure or amorphous phase can be detected in the HRTEM images, further demonstrating the phase purity of the samples.
Fig. 2. FESEM images and particle size statistics of (a-c) Co$_3$O$_4$-AP; (d-f) Co$_3$O$_4$-5 mM; (g-i) Co$_3$O$_4$-10 mM; (j-l) Co$_3$O$_4$-100 mM; (m-o) and Co$_3$O$_4$-1 M samples.

In our previous studies, we used mesoporous Co$_3$O$_4$ nanosheets as precursors to react with NaBH$_4$ solutions [36]. A novel hierarchical nanostructure, i.e., high-density Co$_3$O$_4$ nanoparticles decorated with ultrathin mesoporous Co$_3$O$_4$ nanosheets were obtained after the chemical reduction. *Ex-situ* and *in-situ* studies indicate that the instantaneously formed H$_2$ bubbles in the fresh NaBH$_4$ solution are responsible for the formation of hierarchical structures. In this study, we suppose the continuous generation and collapse of H$_2$ bubbles can act on the Co$_3$O$_4$ nanocubes and induce exfoliation, inducing the formation of thin sheets on the cubes surface.
Fig. 3. TEM, HRTEM images, and SAED patterns (insets) of (a-c) Co$_3$O$_4$-AP; (d-f) Co$_3$O$_4$-5 mM; (g-i) Co$_3$O$_4$-10 mM; (j-l) Co$_3$O$_4$-100 mM; (m-o) and Co$_3$O$_4$-1 M samples.

XPS was employed to achieve a better understanding of surface electronic state and local chemical environment. Fig. 4 presents high-resolution XPS spectra of Co 2p and O 1s regions in the Co$_3$O$_4$ samples. The Co 2p region consists of four peaks that are located at ~780, ~782, ~795, and ~797 eV, respectively. The peaks centered at ~780 and ~795 eV belong to Co$^{3+}$, and the other two peaks attribute to Co$^{2+}$ [37, 38]. Moreover, two satellite peaks (denoted as ‘sat’) can be resolved at the binding energy of ~786 and ~804 eV, which are typical characteristics for the Co$_3$O$_4$ materials. The relative atomic ratio of Co$^{2+}$ to Co$^{3+}$ can be calculated by estimating corresponding
integrated areas in the Co 2p spectra (Fig. 5). The Co$^{2+}$/Co$^{3+}$ value increases from 0.92 (Co$_3$O$_4$-5 mM) to 1.17 (Co$_3$O$_4$-100 mM) and 1.44 (Co$_3$O$_4$-1 M), indicating the increment of Co$^{2+}$ species after the NaBH$_4$ solution treatment. One possible reason can be partial reduction of Co$^{3+}$ to Co$^{2+}$ species after NaBH$_4$ treatment [39, 40]. The O 1s peaks can be best fitted by three components centered at ~529.7, ~531.2, and ~532.8 eV, which can be ascribed to lattice oxygen atoms (O$_L$), oxygen vacancies (O$_V$), and oxygen atoms in surface water molecule (O$_W$), respectively [41-43]. Quantitative studies (Fig. 5) show that the O$_V$/O$_L$ ratio increases from 0.48 in Co$_3$O$_4$-5 mM to 2.39 in Co$_3$O$_4$-10 mM and 2.67 in Co$_3$O$_4$-1 M, demonstrating that more oxygen vacancies are generated in NaBH$_4$ solution with a higher concentration.

**Fig. 4.** High-resolution XPS spectra of Co$_3$O$_4$-AP, Co$_3$O$_4$-5 mM, Co$_3$O$_4$-10 mM, Co$_3$O$_4$-100 mM and Co$_3$O$_4$-1 M samples: (a) Co 2p region, and (b) O 1s region.
**Fig. 5.** The Comparison of Co^{2+}/Co^{3+} (gray), O_v/O_L (red) values and reversible capacities (blue) of different samples (voltage: 0.01 V - 3.0 V, vs. Li^+/Li, current density: 0.1 Ag^{-1}).

The above analysis on microstructure and composition show that oxygen vacancies are formed in the Co_3O_4 nanocubes by chemical reduction treatment in NaBH_4 solutions. Moreover, the amount of oxygen vacancies can be controlled by altering the NaBH_4 concentration. To study the effect of chemical reduction-induced oxygen-deficiency on the lithium storage properties, standard 2032-type coin cells with Co_3O_4 nanocubes as active materials were assembled and tested at room temperature. The typical electrochemical performance of different samples is presented in Fig. 6 and Fig. S1-5. We first investigate CV curves of the first three cycles measured in a potential window of 0.01 - 3 V (vs. Li^+/Li) at a scan rate of 0.5 mVs^{-1}. Generally, the different Co_3O_4 samples show similar electrochemical behavior.
Taking Co$_3$O$_4$-10 mM electrode (Fig. 6a) as an example, a main reduction peak (0.64 V) is observed in the first cathodic scan, and disappears in the next two cycles. The reduction peak can be assigned to the formation of SEI film and Li$_2$O phase. The oxidation peak in the first anodic scan (2.17 V) relates to the delithiation reaction of Co$_3$O$_4$ electrodes. In the second and third cycles, the main reduction peak shifts to a higher potential (1.03 V), which is ascribed to the irreversible structure change of the Co$_3$O$_4$ electrodes when lithium ions are firstly introduced. Similar results have also been reported in previous studies [44-46]. In the subsequent two cycles, the CV curves overlap very well, demonstrating the stability of Co$_3$O$_4$ electrode after the initial charge-discharge cycling [36, 47, 48]. Fig. 6b shows galvanostatic charge-discharge curves of Co$_3$O$_4$-10 mM electrode for the first three cycles at 0.1 Ag$^{-1}$ in the cut-off potential window of 0.01 - 3 V (vs. Li$^+$/Li). In the first discharge process, there is a typical voltage plateau appearing at ~1.1 V and a slope when voltage increases, these features are related to the conversion reaction of Co$_3$O$_4$ electrode and the formation of SEI film, respectively. In the charge step, the voltage plateau at ~2.0 V is related to the oxidation reaction of Co$_3$O$_4$ electrodes [49, 50]. The following two charge-discharge processes tend to be stable, which are in agreement with the CV results (Fig. 6a). The first charge capacity is 890.2 mAhg$^{-1}$ and is much lower than the first discharge capacity of 1192.1 mAgh$^{-1}$, leading to the initial Coulombic efficiency of 74.7%. This irreversible capacity loss is attributed to the formation of SEI film and electrolyte decomposition in the first discharge process [51, 52]. It can also be observed that Co$_3$O$_4$-10 mM sample exhibits the best
electrochemical performance (Fig. S1-5). Specifically, Fig. 6c compares the cycling stability of the samples evaluated at a current density of 0.1 Ag⁻¹ up to 50 cycles. The Co₃O₄-10 mM cell exhibits much better cycling performance, and possesses the highest lithium storage capacity. After 50 cycles, the reversible capacity of Co₃O₄-10 mM cell reaches 873.5 mAhg⁻¹, which is higher than that of Co₃O₄-5 mM (764.3 mAhg⁻¹), Co₃O₄-AP (705.3 mAhg⁻¹), Co₃O₄-100 mM (559.7 mAhg⁻¹), and Co₃O₄-1 M (322.3 mAhg⁻¹, see also Fig. 5). Rate performance of the Co₃O₄ electrodes was evaluated at different current densities between 0.1 and 5 Ag⁻¹ as shown in Fig. 5d. The capacities of the Co₃O₄-10 mM cell are 954.1, 886.2, 831.5, and 569.1 mAhg⁻¹ at the current densities of 0.1, 0.5, 1, and 5 Ag⁻¹, respectively. When the current density is settled back to the initial value of 0.1 Ag⁻¹ after 40 cycles, the capacity can go back to the original level. After the cycling test (50 cycles), the morphology of the Co₃O₄-10 mM electrode was characterized by FESEM (Fig. S6). The sample basically preserves the initial morphology, demonstrating the structural stability during charge-discharge cycling. In contrast, the other samples exhibit obvious capacity attenuation at the studied current densities. The results reveal that the lithium storage properties of Co₃O₄ electrodes can be optimized by tuning oxygen deficiency amount through chemical reduction (Fig. 5).
**Fig. 6.** Lithium storage properties of the samples. (a) CV curves of the Co$_3$O$_4$-10 mM electrode for the first three cycles between potential window of 0.01 - 3 V (vs. Li$^+/\text{Li}$) at a scan rate of 0.5 mVs$^{-1}$; (b) Galvanostatic charge-discharge voltage profiles of the Co$_3$O$_4$-10 mM for the first three cycles between 0.01 and 3 V (vs. Li$^+/\text{Li}$) at a current density of 0.1 Ag$^{-1}$; Comparison of (c) cycling stability and (d) rate capability of the Co$_3$O$_4$-AP, Co$_3$O$_4$-5 mM, Co$_3$O$_4$-10 mM, Co$_3$O$_4$-100 mM and Co$_3$O$_4$-1 M electrodes.

To determine more kinetics parameters of the as-prepared and solution treated Co$_3$O$_4$ nanocubes, we performed EIS measurements for the Co$_3$O$_4$-10 mM and Co$_3$O$_4$-AP electrodes before and after cycling test (the EIS results for other electrodes are shown in Fig. S7-S9). Fig. 7 displays the typical Nyquist plots. The intercept ($R_s$) at high-frequency is associated with the electrical resistance of the electrolyte. The semicircle diameter represents the charge-transfer resistance ($R_{ct}$), which is related to the resistances at active material-current collector and electrode-electrolyte interfaces.
The linear plot in the low-frequency range is ascribed to Warburg impedance ($Z_w$), which is attributed to the ion diffusion in the electrodes [43, 50]. The kinetic parameters can be derived by modeling the impedance spectra using an equivalent circuit (Fig. 7b inset). Of all the parameters, $R_{ct}$ value directly relates to the rate performance of the electrodes [53-55]. The fitted $R_{ct}$ values of Co$_3$O$_4$-10 mM and Co$_3$O$_4$-AP electrodes are shown in Fig. 7c. Before cycling, the $R_{ct}$ value of Co$_3$O$_4$-10 mM electrode is 856.1 $\Omega$, which is smaller than that of Co$_3$O$_4$-AP electrode (2264 $\Omega$). After 50 cycles, the two electrodes exhibit smaller $R_{ct}$ values than that of the fresh ones, and the $R_{ct}$ value of Co$_3$O$_4$-10 mM (696.6 $\Omega$) is smaller than Co$_3$O$_4$-AP electrode (1281 $\Omega$). Therefore, the Co$_3$O$_4$-10 mM electrode possesses smaller resistance, which facilitates ion transportation for a higher utilization of the electrode, especially under high rate discharge conditions.

Fig. 7. Nyquist plots of Co$_3$O$_4$-AP and Co$_3$O$_4$-10 mM electrodes (a) before and (b) after 50 charge-discharge cycles; (c) The bar chart of $R_{ct}$ resistance before and after cycling. The spectra were measured with an amplitude of 10 mV over the frequency range of 1 mHz and 100 kHz. The inset of (a) shows the equivalent electrical circuit used for fitting the EIS data. $R_s$ is the electrolyte resistance, $R_{ct}$ is the charge-transfer resistance, $Z_w$ is the Warburg impedance, and CPE is the constant phase-angle
Combining the above microstructure, chemical composition, and electrochemical analysis, we attribute the good lithium storage properties of the $\text{Co}_3\text{O}_4$-10 mM electrode to the following possible reasons: (1) chemical reduction-induced oxygen deficiency improves the intrinsic conductivity of $\text{Co}_3\text{O}_4$ electrodes, and accelerates the ion and electron transportation during cycling; (2) the oxygen deficient structures also allow for storing more ions and a higher capacity can thus be achieved; (3) the $\text{Co}_3\text{O}_4$ nanocubes possess good mechanical strength to accommodate the volume changes during the continuous charging-discharging operations, which is of importance to keep the structural and cycling stability; (4) further increasing the concentration of $\text{NaBH}_4$ solution (above 10 mM) degrades the crystallinity of $\text{Co}_3\text{O}_4$ electrodes, and destroys the cyclic stability and rate performance. It is therefore essential to balance oxygen deficiency and crystallinity during chemical reduction treatment to design and synthesize high-performance electrodes.

4. Conclusions

In this work, we present a detailed study of microstructure, chemical composition, and electrochemical lithium storage properties of $\text{Co}_3\text{O}_4$ nanocubes modified by chemical reduction treatment in $\text{NaBH}_4$ solutions. Structural characterizations indicate that the treated $\text{Co}_3\text{O}_4$ nanocubes are oxygen deficient, while the cubic morphology and particle size are preserved. Moreover, the degree of oxygen deficiency can be controlled by altering the concentration of $\text{NaBH}_4$ solution.
When evaluated as anodes for LIBs, the optimized sample (Co$_3$O$_4$-10 mM) shows the best lithium storage properties. Specifically, a reversible capacity of 873.5 mAh$^{-1}$ is measured after 50 cycles at a current density of 0.1 Ag$^{-1}$, and a charge-discharge capacity of 569.1 mAh$^{-1}$ is achieved at a higher current density of 5 Ag$^{-1}$. Thanks to the facile modification strategy and potential for mass production, chemical reduction can be a promising way to generate controlled defects in functional nanostructures for a wide range of energy applications.

**Acknowledgments**

This work was supported by National Natural Science Foundation of China (No. 51571054, 51771046, 51674068, 51871046).

**References**


