Integrated Co₃O₄/TiO₂ Composite Hollow Polyhedrons Prepared via Cation-exchange Metal-Organic Framework for Superior Lithium-ion Batteries

Wangwang Xu, Xiaodan Cui, Zhiqiang Xie, Grant Dietrich, Ying Wang

Department of Mechanical & Industrial Engineering, Louisiana State University, Baton Rouge, LA 70803, USA

Abstract

Co₃O₄, as an attractive lithium ion battery anode material, though benefited from its high theoretical capacity, has long suffered from low electrical transportation and dramatic volume variations. Therefore, to develop a LIB anode material with both good capability and excellent stability, rational design of composite material is becoming an appealing method. Herein, we report a scalable method of fabricating integrated Co₃O₄/TiO₂ composite hollow polyhedrons through a cation-exchange approach in metal-organic framework. In this synthesis, well-defined ZIF-67 particles not only serve as the host to accommodate exchanged titanium cations but also the template to form hollow polyhedron structure. The obtained integrated Co₃O₄/TiO₂ composite hollow polyhedrons exhibit a high reversible capacity of 642 mAh/g at a rate of 500 mA/g after 200 cycles, accounting for 96.9% of the initial capacity, much higher than that of pure Co₃O₄, which only maintain a specific capacity of 200 mA/h and a capacity retention of 40%. The optimized integrated Co₃O₄/TiO₂ composite hollow polyhedrons display significant improvements in electrochemical performance, demonstrating great potential as advanced anode material for future lithium ion batteries.

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1. Introduction

The present increasing energy demand for energy storage system with high efficiency, environmental benignity and low cost has stimulated intense research on lithium-ion batteries (LIBs) [1]. Since its invention in 1991, rechargeable LIBs have gradually dominated the market of portable energy storage devices and shown great promise to satisfy the fast-increasing energy demand of a sustainable and environmentally-friendly society [2–5]. However, limited energy density and capacity of LIBs have fallen short of our expectations in expanding their applications to a broader field, especially hybrid electric vehicles (HEVs) and electric vehicle (EVs), where high energy density and large capacity are essential. [6,7] In order to enhance the capacity and energy density of LIBs, a great deal of research has been centered on the development of novel anode materials with larger theoretical capacity, lower cost, better stability as well as durability [8,9].

So far, many materials have been exploited as anode materials for LIBs, such as nitrogen-doped/graphitic carbon [10], metal oxides (MnO₂ [11], Fe₂O₃ [12], Co₃O₄ [13], NiO [14], MoO₂ [15], SnO₂ [16,17], TiO₂ [18]), metal sulfides (MoS₂ [19], SnS₂ [20], CoS [21], VS₂ [22], and lithium alloys (Sn, Si, Sb)/multinary alloys [23–25]. Among them, Co₃O₄ is considered as one of the most promising anode material in LIBs due to its large theoretical capacity (890 mAh/g), which is more than two times that of current commercially used graphite anode (372 mAh/g) [26]. Therefore, Co₃O₄ is expected to satisfy the future large energy-storage demand. However, accompanying superior lithium storage capacity, Co₃O₄ also suffers from its limitations of (a) poor electronic conductivity, and (b) serious electrode pulverization resulted from its large volume expansion/contraction during cycling. In the Li insertion and extraction process, severe volume change associated with particle crush, lead to large irreversible capacity loss and poor capacity retention, hindering Co₃O₄-based anodes from commercial applications. Over the years, extensive efforts have been focused on addressing the first issue of poor electronic conductivity, via fabricating nanostructures hybridized with conducting materials, including amorphous carbon, graphene oxide nanosheet and conductive polymers, in an attempt to improve electronic
conductivity and structure stability of CoOx. For example, as reported by Lin et al., peapod-like CoOx@carbon nanocomposites can supply the specific capacity of as high as 1050 mAh/g, which is much higher than that of single CoOx nanoparticles (372 mAh/g) after 50 cycles at specific current of 1C [27]. Moreover, CoOx@carbon nanotube arrays, reported by Scitih et al., can provide the specific capacity of 700 mAh/g at 10 mA/g after 100 cycles, which is far more than that of the pure CoOx (199 mAh/g) [28]. Their work makes great progress on improving the conductivity of CoOx and its structural stability to a certain extent. However, insufficient emphasis has been placed on overcoming the second challenge—severe volume change during lithiation and delithiation due to volume expansion of inner CoOx, which causes the protective coating layer to crack and fracture, rendering the original core–shell structure. The volume change associated with particle crush leads to large irreversible capacity loss and poor capacity retention, hindering commercial applications of CoOx-based anodes.

Another transition metal oxide, TiO2, more specifically, anatase–TiO2, has received increasing attention as novel anode material for LIBs due to its low cost, good cycling stability as well as environmentally friendly quality [29]. In comparison with most transition metal oxides, anatase–TiO2 displays better cycling ability because of its relatively low theoretical capacity (178 mAh/g) and fewer inserted amorphous of lithium ions. Moreover, due to its excellent structural stability, TiO2 can also act as a promising protective layer for active material to maintain mechanical integration during cycling. For example, Cui et al. designed sulphur-TiO2 yolk-shell nanoarchitecture [30]. The sulphur-TiO2 yolk-shell nanoarchitecture displays an initial capacity of 1030 mAh/g at 0.5C and a capacity decay as small as 0.033% per cycle after 1000 cycles, presenting superior cycling ability. Such remarkable performance is attributed to the stable TiO2 shell and novel yolk-shell nanoarchitecture. Moreover, as reported in previous reports, in comparison with pure TiO2 and transition metal oxides, TiO2/transition metal oxides composite exhibit enhanced electrochemical performances due to the positive synergistic effect. [31–33] The electrochemical performance of the composite with different ratio of TiO2 and transition metal has also been explored. [31–35] The composite with a higher mass content of TiO2 usually exhibits a relative lower initial capacity with better cyclability. For example, Liu et al. reported that CoOx/TiO2 composite with a mass ratio of 6:1, exhibits limited improved cyclability over 150 cycles compared to pure CoOx [32]. Moreover, Jau mann et al. reported the CoO/TiO2 composite with a very high TiO2 content (>50%) that shows excellent cycle ability but very low capacity. [35] In this respect, the strategy of designing composite nanoarchitecture with stable TiO2 and large-capacity metal oxides can help one realize synergic property of electrochemistry.

Metal–organic frameworks (MOFs), composed by metal clusters with electron-donating organic ligands, have been intensively studied as a result of their versatile structural topologies, tunable functionalitites, as well as wide applications in catalysis, gas storage, and biomedical imaging. In recent years, cation exchange has emerged as an effective synthetic route to the modification of secondary building units of MOFs [36]. According to Ringwood’s rule [37], ions with similar electronegativity could replace each other. The ions with the lower electronegativity will be exchanged more easily because it can form stronger bonds with the one with larger ionic character. Recently, it has been widely used to improve chemical/physical properties of molecules and nanocrystals, expanding the applications of MOFs. For example, Rosi et al., reported that their CO2 adsorption properties can be tuned by cation exchange. Because the pore size of MOF-1 can be synthetically modified via straightforward cation-exchange experiments, such modifications can be used to tune the CO2 adsorption capacity of MOF-1 [38]. Moreover, the cation exchange process can also be used to synthesize composite heterostructures. Hollingsworth et al. have synthesized PbSe/CdSe core/shell quantum dots using a controllable partial cation exchange method. The resulted core/shell nanocrystal quantum dots are stable against fading and spectral shifting due to the synergic physical properties [39].

Herein, we report for the first time, the controllable design of CoOx/TiO2 composite hollow polyhedron nanoarchitecture via cation exchange in zeolitic imidazolate frameworks (ZIF-67), followed by thermal treatment. Co2+ cation can be replaced by Ti4+ cation more easily than Co3+ due to its lower electronegativity. The CoOx/TiO2 composite hollow polyhedrons display prolonged and stable cycling for over 200 cycles as anode material for LIBs. The unique advantage of such composite hollow polyhedrons lies in the synergistic effect of two integrated components as anode material for LIBs. Specifically, CoOx can supply durable large capacity at high specific current, due to the integration of TiO2 with stable structure and higher conductivity. Moreover, the internal void space can effectively accommodate large volumetric expansion of CoOx during cycling, maintaining structural integrity of the shell. In addition, owing to better conductivity, the TiO2 component provides faster pathways for electron transportation, improving electrochemical reaction kinetics of the composite. In comparison with bare CoOx hollow polyhedrons, the composite nanostructures are found to exhibit superior capacity retention and rate capability. At a specific current of 500 mA/g, the composite nanostructures provide an initial capacity as high as 662 mAh/g, and maintain a stable capacity of 642 mAh/g after 200 cycles, accounting for 96.9% of the initial capacity, much higher than pure CoOx hollow polyhedrons that can only maintain a specific capacity of 200 mAh/g and a capacity retention of only 40%. To the best of our knowledge, this is the first time that CoOx with this level of performance has been reported for application as LIB anode material.

2. Experimental Section

2.1. Synthesis of ZIF-67

1.97 g of 2-methylimidazole was dissolved in mixed solvent of methanol (20 ml) and ethanol (20 ml). Then, 1,746 g Co(NO3)2·6H2O was dissolved in another mixed solvent of methanol (20 ml) and ethanol (20 ml). After stirring for 10 minutes, the above two solutions were mixed and kept stirring for 20 hours at 25 °C [40]. The purple products were collected by centrifugation, washed with ethanol for three times, and finally dried at 80 °C for 12 hours in air.

2.2. Synthesis of Composite Co3O4/TiO2 Hollow Polyhedrons via Cation-exchange

Tetrabutyl titanate (6 mmol) was dissolved in 100 ml dry deaerated DMF. After being stirred for 10 mins, 100 mg ZIF-67 was dispersed in the solution. The suspensions were stirred gently for 48 hours at room temperature (25 °C). After the exchange of Ti4+ cations, the precipitates were collected by centrifuge and rinsed with DMF and alcohol several times, and dried at 80 °C for 12 h. Finally, the product was obtained by annealing the powder at 300 °C with a heating rate of 2 °C/min and kept at that temperature for 2 h.

2.3. Synthesis of Co3O4 Hollow Polyhedrons

The ZIF-67 polyhedrons were dispersed in a crucible, heated to 300 °C with the heating rate of 2 °C/min and kept at that temperature for 2 h in the furnace. After that, the furnace is cooled down to room temperature naturally.
2.4. Characterization

The chemical states of obtained products were studied by X-ray photoelectron spectroscopy (XPS). XPS data were collected on an AXIS165 spectrometer using a twin-anode Al Kα (1486.6 eV) X-ray as the excitation source with the charge neutralization function being turned on. Crystallographic structure were determined by Rigaku MiniFlex X-ray diffraction (XRD) measurement with Cu Kα radiation(λ = 1.5405 Å) in a 2θ range from 10° to 90° with scanning rate of 1°/min. Energy dispersive spectroscopic (EDS) as well as sample morphology were characterized by a FEI Quanta 3D FEG field emission scanning electron microscope (FESEM) and a JEM-1400 transmission electron microscope (TEM).

2.5. Electrochemical Measurements

The working electrode was prepared by casting a mixture consisting of as-prepared Co3O4/TiO2 composite hollow polyhedrons, or pure Co3O4 hollow polyhedrons, carbon black and sodium alginate binder mixed at a weight ratio of 7:2:1 in deionized water onto a copper foil with a doctor blade, followed by drying at 70 °C. CR2032-type coin cells were assembled in an argon filled glove-box, using lithium foil as the counter electrode, Celgard-2320 membrane as the separator, and 1 M LiPF6 dissolved in dimethyl carbonate (DMC)/ethylene carbonate (EC)/diethylcarbonate (DEC) at a volumetric ratio of 1:1:1 as the electrolyte, then followed by 12 h aging treatment before electrochemical measurements. Galvanostatic charge/discharge experiment were carried out on an eight-channel battery analyzer (MTI Corporation) between 0.01 V and 3.00 V versus Li+/Li. Cyclic voltammetry (CV) measurements were conducted on an electrochemical work station (CHI 6504C) over the potential range of 0.01–3.00 V vs. Li+/Li at 0.1 mV/s scanning rate. Electrochemical impedance spectroscopy (EIS) measurements were operated by applying an AC potential of 5 mV amplitude in the frequency range from 0.01 to 100 kHz.

3. Result and Discussion


The fabrication procedure of Co3O4/TiO2 composite hollow polyhedrons is illustrated in Fig. 1. The ZIF-67 hollow polyhedrons were prepared by a precipitation method with the precursors of cobalt nitrite and 2-methylimidazole in methanol for 20 hours at room temperature. Then, cation exchange took place on the surface of ZIF-67 in the solvent of dimethyl formamide. Ti4+ has much lower electronegativity than that of Co2+. Therefore, it is remarkable that they can undergo the cation exchange [36], which is described in the following steps. First, when ZIF-67 hollow polyhedrons are completely surrounded by the solvent of dimethyl formamide, the inorganic clusters of ZIF-67, also called secondary-building units, will be partially solvated. Then, the bond between the cluster and Co2+ cations starts to break, and gradually bound with Ti4+ cations. In this process, the solvent molecules step-wisely connect to Co2+ cations as they remain partially bound to the cluster. Next, Ti4+ cations partially replace Co2+ cations in the secondary building units, forming Ti4+-exchanged ZIF-67 [12]. Finally, the composite Co3O4/TiO2 hollow polyhedrons are yielded through decomposition and oxidation of Ti4+ exchanged ZIF-67 via sintering in air for two hours. For comparison purpose, pure Co3O4 hollow polyhedrons are synthesized by annealing ZIF-67 directly.

In order to examine the stability of Ti4+ exchanged ZIF-67, crystal structure of the products formed at each step is determined by XRD, as shown in Fig. S1. Fig. S1 displays XRD pattern of ZIF-67 and Ti4+ exchanged ZIF-67 hollow polyhedrons. It is found that all the typical diffraction peaks from (011), (002), (112) and (222) planes, are consistent with previous reports [40]. Moreover, the Ti4+ exchanged ZIF 67 displays the same peak positions as those from ZIF-67, indicating that ZIF 67 is stable and flexible enough to accommodate the exchanging Ti4+ cations. To confirm the Ti4+ cations exchanged in ZIF-67, XPS studies were carried out and the

Fig. 1. The ZIF-67 sample possesses a hollow polyhedron structure. After cation exchange with Ti4+, ZIF-67 is converted into Ti4+/Co2+ composite ZIF-67. Then Co3O4/TiO2 composite hollow polyhedrons are obtained after thermal annealing in air. For comparison purpose, pure Co3O4 hollow polyhedrons are obtained without cation exchange.

results are shown in Figs. 2a and S2. Fig. 2a displays the survey scan spectra of ZIF-67 and Ti4+ exchanged ZIF-67. The XPS spectrum of ZIF-67 from XPS analysis exhibits the principal C1s, O1s, N1s and Co2p3/2 core levels, with no impurities. After exchanging with Ti4+ cations, the XPS spectrum of Ti4+ exchanged ZIF-67 reveals the addition of Ti 2p3/2 peak, confirming successful exchanging of Ti4+ cations in ZIF-67. Detailed scans of the Co 2p range and Ti 2p range are illustrated in Fig. S2a and b respectively. In the Co 2p XPS spectra, the Co 2p3/2 and Co 2p1/2 components are distinct along with two satellite peaks. The Co 2p3/2 and Co 2p1/2 peaks, located at binding energies of 780.5 and 795.4 eV, respectively, are characteristic of Co2+ species. In the Ti 2p spectra, there are two peaks, Ti 2p3/2 and Ti 2p1/2, centering at 457.9 and 463.7 eV respectively, in accordance with Ti4+ species.

The crystal structures of Co3O4 hollow polyhedrons and Co3O4/TiO2 composite hollow polyhedrons are also determined by XRD, as shown in Fig. 2b. After sintering in air, XRD analysis indicates ZIF-67 hollow polyhedrons are completely converted into Co3O4 hollow polyhedrons, as displayed in Fig. 2b. Co3O4 hollow polyhedrons are identified as cubic cobalt oxide with lattice parameters a = b = c = 8.056 Å, Fd-3 m space group, which is in good agreement with standard XRD patterns of cubic Co3O4 (JCPDF card

Fig. 3. SEM images of (a) ZIF-67 hollow polyhedrons, (b) Ti4+ exchanged ZIF-67 hollow polyhedrons, (c) Co3O4/TiO2 composite hollow polyhedrons, (d) SEM image of Co3O4/TiO2 composite hollow polyhedrons and corresponding EDS mappings of O, N, C and Sn elements.
As for the Co3O4/TiO2 composite hollow polyhedrons, their XRD pattern displays mixture of cubic Co3O4 and anatase TiO2. The as-formed TiO2 is identified as cubic anatase TiO2, with lattice parameters of a = 3.6486 Å, b = 3.6486 Å, c = 5.8992 Å, which match well with those of standard XRD patterns of cubic anatase TiO2 (JCPDF card no. 01-076-1802) [42]. The co-existence of cubic Co3O4 and anatase TiO2 confirms the formation of Co3O4/TiO2 composite structure.

In order to investigate the morphology of the products in each step, their FESEM images have been taken and displayed in Fig. 3. Fig. 3a manifest the SEM image of the well-defined ZIF-67 hollow polyhedrons. In Fig. 3a, the size and polyhedral shape of ZIF-67 nanoparticles are quite uniform. As can be seen in the inset magnified SEM image in Fig. 3a, ZIF-67 hollow polyhedrons are about 200 nm in width. As displayed clearly in Fig. 3b, the size and polyhedral shape of ZIF-67 nanoparticles are retained well after the cation exchange with Ti4+ for about two days, except that the surface of the polyhedrons becomes slightly rougher. To explore the influence of the concentration of titanium source, the cation-exchange process was also taken in a tetrabutyl titanate concentration as high as 12 M. As seen in Fig. S3, the polyhedral shape of the sample is maintained at a high concentration of titanium source, indicating that ZIF-67 particles are stable enough to accommodate the inserted titanium cations. After thermal treatment, the Co3O4/TiO2 composite is obtained with the retained hollow-polyhedron shape, as displayed in Fig. 3c. Also in Fig. 3c, many tiny nanoparticles are observed on the rough surface. Moreover, in Fig. 3d, some broken polyhedral particles display open voids, indicating well maintained hollow structures of ZIF-67. It can be seen that the Co3O4/TiO2 composite hollow polyhedrons, with a thickness of about 20 nm, are composed of closely interconnected nanoparticles. The composition of Co3O4/TiO2 composite hollow polyhedrons is also confirmed by EDS mapping. EDS of the elemental mappings is performed on the sample of Co3O4/TiO2 composite hollow polyhedrons and the results are shown in Figs. 3 d and S4. The cobalt, titanium, and oxygen signals overlap uniformly across the entire sample, indicating uniform formation of Co3O4/TiO2 composite hollow polyhedrons. The mass ratio of Co3O4 and TiO2 is about 8:2. The corresponding SEM image, EDS, and XRD pattern clearly demonstrate the morphology and structure of Co3O4/TiO2 composite hollow polyhedrons.

In order to further identify the microstructure and crystallographic relationship of TiO2 and Co3O4, TEM and HRTEM imaging are carried out on the two samples. The TEM images of Co3O4/TiO2 composite hollow polyhedrons in Fig. 4a reveal their microstructure, confirming the uniform polyhedral morphology and the inner void of the composite hollow polyhedrons. To explore more details of the sample, Fig. 4b presents the corresponding HRTEM image of the circled area in the insert TEM image. The HRTEM image reveals the polycrystalline nature of Co3O4/TiO2 composite hollow polyhedrons, which are composed of interconnected nanoparticles with a diameter of about several nanometers. The HRTEM image in Fig. 4b exhibits lattice fringes with different d-spacings of 4.66 Å and 2.33 Å, corresponding to the (111), (220) and (222) planes of cubic Co3O4 crystals. On the edge of composite hollow polyhedrons, lattice fringes with the d-spacings of 2.37 Å are in good agreement with the interplanar spacings of anatase TiO2, indicating the formation of TiO2 grains during thermal treatment.

3.2. Electrochemical Performance

To evaluate electrochemical performances of all the samples, coin cells of Co3O4/TiO2 composite hollow polyhedrons and pure Co3O4 hollow polyhedrons cycled in a voltage range of 0.01–3 V versus Li+/Li. As a novel composite anode material for LIBs, cyclic voltammetry (CV) profile of Co3O4/TiO2 composite hollow polyhedrons is carried out at a scan rate of 0.1 mV/s in a potential region of 0.01–3 V to explore the lithium insertion/extraction behaviors. The electrochemical reactions of Co3O4 and TiO2 with lithium are described below:

\[ \text{Co}_3\text{O}_4 + 8\text{Li}^+ + 8\text{e}^- = 4\text{Li}_2\text{O} + 3\text{Co} \]  

(1)

\[ \text{TiO}_2 + x\text{Li}^+ + x\text{e}^- = \text{Li}_x\text{TiO}_2 (x \leq 1) \]  

(2)

Fig. 5a displays the CV curves of Co3O4/TiO2 composite hollow polyhedrons. In the first cathodic scan, a small peak at around 1.08 V vs. Li+/Li is ascribed to the irreversible insertion of lithium ions to form the Li3Co3O4 phase. During the continuous discharge process, the prominent potentials at around 0.85 V is observed, corresponding to destruction of crystal structure and formation of solid–electrolyte interphase (SEI) films. During the following anodic scan, a broad peak located at about 2.13 V vs. Li+/Li is ascribed to the re-oxidation of metallic cobalt and the decomposition of Li2O according to the reversible conversion mechanism described by the equation (reaction (1)). In subsequent cycles, three cathodic peaks and one broad anodic peak can be clearly observed. The characteristic cathodic peak at 1.7 V and anodic peak at 2.0 V are attributed to the lithium intercalation/extraction into/from anatase TiO2 (reaction (2)). The broad anodic peak at 2.13 and two cathodic peaks at 1.3 and 0.9 V are associated with the reversible oxidation/reduction of Co/Co3O4 (reaction (1)). The anodic peak of TiO2 at 2.0 V is overlapped by the anodic peak of Co3O4, forming a broad peak located at 2.13 V. Fig. 5b exhibits the voltage profiles of the Co3O4/TiO2 composite for the first three cycles. The identified charge-discharge platforms are consistent.
with the result of the CV analysis above. In Fig. S5, the broad sloping plateau at 0.8–1.1 V may be related to the initial reduction of Co$_3$O$_4$ to Co, and the formation of irreversible solid electrolyte interphase (SEI) film. It is observed that the initial discharge and charge capacities of the Co$_3$O$_4$/TiO$_2$ composite are 662 and 535 mAh/g, respectively. The initial capacity loss of 19% may be mainly ascribed to the irreversible processes such as electrolyte decomposition, the formation of SEI films and undecomposed Li$_2$O phase, which are commonly observed for most anode materials.

[43–47] Fig. Sb compares cycling performances of Co$_3$O$_4$/TiO$_2$ composite hollow polyhedrons and pure Co$_3$O$_4$ hollow polyhedrons when cycled at a specific current of 500 mA/g. It is found that Co$_3$O$_4$/TiO$_2$ composite hollow polyhedrons exhibit an unexpected but interesting cycling performance. It is observed that at a specific current of 500 mA/g, the initial discharge capacity of pure Co$_3$O$_4$ hollow polyhedrons is 730 mAh/g, higher than that of Co$_3$O$_4$/TiO$_2$ composite hollow polyhedrons (662 mAh/g). Such phenomenon is attributed to the larger theoretical capacity of Co$_3$O$_4$ than that of TiO$_2$. After 200 cycles, Co$_3$O$_4$/TiO$_2$ composite hollow polyhedrons keep a reversible capacity of 642 mAh/g, maintaining 96.9% of the initial capacity, demonstrating a very large discharge capacity and outstanding cycling stability. In contrast, the reversible capacity of pure Co$_3$O$_4$ hollow polyhedrons electrode drops rapidly from 730 to 350 mAh/g, corresponding to a very low capacity retention of 44.9%. This serious capacity fading of pure Co$_3$O$_4$ hollow polyhedrons may be caused by expansion/contraction during charge/discharge, leading to severe pulverization and delamination from the underlying current collector. Notably, the specific capacity of the Co$_3$O$_4$/TiO$_2$ composite electrode decreases for the initial 10 cycles and then increases in subsequent cycles. For various nanostructured transition metal-oxide electrodes, this phenomenon of the initial increased capacity is widely observed [45–47]. During the charge-discharge process, the decomposition of the electrolyte leads to formation of an electrochemically gel-like polymer layer on the surface of active materials, which can enhance the Li-ion storage capacity through a so called “pseudo-capacitance-type behavior” [48]. Another possible reason is that Co nanoparticles may be formed at the interface of Co$_3$O$_4$/TiO$_2$ due to some irreversible electrochemical reaction and the presence of Co may improve the reversibility of electrochemical reaction of active material, resulting in improved specific capacity [49]. In Fig. Sc, the rate performance of the two samples is evaluated at various specific current ranging from 50 to 2000 mA/g. Co$_3$O$_4$/TiO$_2$ composite hollow polyhedrons exhibit a better rate capability than that of pure Co$_3$O$_4$ hollow polyhedrons, especially at high rates. They deliver average discharge capacities of 710, 630, 550, 480 and 400 mA/h at 50, 200, 500, 1000, and 2000 mA/g, respectively. It is clearly observed that even when the specific current is as high as 2000 mA/g, about 390 mA/h of the capacity is still retained, much higher than pure Co$_3$O$_4$ as well as commercial graphite anode. More importantly, when the specific current returns from 2000 mA/g to 50 mA/g, its discharge capacity recovers to 710 mAh/g immediately and maintains a good capacity retention in the following cycles, indicating very good rate capability of the material. Fig. Sd displays galvanostatic charge/discharge curves of the Co$_3$O$_4$/TiO$_2$ composite hollow polyhedrons electrode at specific currents of 100, 500, 1000, 2000, 2000 and 100 mA/g, corresponding to the rate performance. The discharge and charge potential plateaus of each cycle are consistent with corresponding CV redox peaks. The high capacity, long cycling life and excellent rate capability of Co$_3$O$_4$/TiO$_2$ composite hollow polyhedrons can be attributed to the stable composite structure and high conductivity.
Moreover, structural integrity after repeated cycling is a major issue in rechargeable lithium batteries. To examine this aspect, the impedance of the electrode is evaluated after 100 electrochemical cycles, and the EIS results are shown in Fig. 6a. EIS technology, one of the most powerful tools for studying electrochemical kinetics, can be used to investigate the processes occurring at the electrode/electrolyte interfaces and Li\(^+\) intercalation/de-intercalation within electrode materials in the battery cells. In the Nyquist plots, \(R_\Omega\) represents the Ohmic resistance of the battery cell, including electrodes, electrolyte and other cell components. \(R_T\) represents the charge transfer resistance. \(CPE\) and \(Z_n\) are the double layer capacitance and the Warburg impedance, respectively. The Nyquist plots of all the three electrodes are composed of a depressed semicircle in the medium-frequency region followed by a slanted line in the low-frequency region. The charge transfer resistance of Co\(_3\)O\(_4\) hollow polyhedrons is around 125 \(\Omega\). After being integrated with TiO\(_2\), the resistance is decreased to 100 \(\Omega\), indicating faster charge transfer at the electrode/electrolyte interface for Co\(_3\)O\(_4/\) TiO\(_2\) composite hollow polyhedrons. After 100 electrochemical cycles, the charge-transfer resistance is further decreased to 75 \(\Omega\), owing to the formation of cobalt after irreversible reactions. As for the morphology change, SEM images of Co\(_3\)O\(_4/\)TiO\(_2\) composite hollow polyhedrons after 200 cycles are shown in Fig. 6b. It can be seen the electrode retains its original hollow polyhedrons architecture after 200 cycles. Although the repeated lithiation and delithiation of Co\(_3\)O\(_4\) can result in large volume change during cycling, the hollow polyhedral shape is well maintained. In comparison with usually observed collapse of Co\(_3\)O\(_4\) electrode, Co\(_3\)O\(_4/\)TiO\(_2\) composite hollow polyhedrons is remarkably stable.

Finally, the advantages of the novel composite nanostructure electrode are described below. The remarkable performance of the new electrode is attributed to the composite hollow polyhedron structure. First, the uniform integration of titanium ions by cation exchange in ZIF-67, and the simultaneous decomposition and crystallization of TiO\(_2\) contribute the formation of integrated Co\(_3\)O\(_4/\)TiO\(_2\) composite hollow polyhedrons during sintering. The integration of Co\(_3\)O\(_4/\)TiO\(_2\) composite promotes the robust stability of hollow polyhedrons nanostructure. Second, the void hollow structure not only facilitates penetration of electrolyte, but also accommodates large volumetric expansion of Co\(_3\)O\(_4\) during cycling. Third, the strategy of integration of Co\(_3\)O\(_4\) and TiO\(_2\) can realize synergic property of electrochemistry. As a result of these beneficial factors, the Co\(_3\)O\(_4/\)TiO\(_2\) composite hollow polyhedrons improve the cycling life up to 200 cycles.

4. Conclusion

In summary, this report has demonstrated a scalable and controllable approach for fabricating Co\(_3\)O\(_4/\)TiO\(_2\) composite hollow polyhedrons through a cation-exchange strategy followed by thermal treatment. During the synthesis process, ZIF-67 polyhedrons not only act as a host for the exchanged titanium cations, but also serve as the template for the formation of the hollow framework of Co\(_3\)O\(_4/\)TiO\(_2\) composite. In such a structure, TiO\(_2\) provides a stable backbone to supply the high capacity of Co\(_3\)O\(_4\) durably. In addition, TiO\(_2\) also served as conductive path for higher transportation of electrons. The as-prepared Co\(_3\)O\(_4/\)TiO\(_2\) composite hollow polyhedrons exhibit long cycling life and remarkable rate capability. At a specific current of 500 mA/g, the composite nanostructures can provide the initial capacity as high as 662 mAh/g, and maintain a stable capacity of 642 mAh/g after 200 cycles, accounting for 96.9% the initial capacity, much higher than that of pure Co\(_3\)O\(_4\) hollow polyhedrons, which can only maintain a specific capacity of 200 mAh/g and a capacity retention of only 40%. Furthermore, the novel cation exchange strategy in this work can be extended to construction of more complex composite nanostructure for broader applications in solar cells, Supercapacitor and fuel cells.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. electacta.2016.11.071.

References


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