



# Physicochemical identity and charge storage properties of battery-type nickel oxide material and its composites with activated carbon



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## ABSTRACT

The structural properties of annealed nickel oxide and its composites with activated carbon (synthesized via simple precipitation methods) have been addressed using X-ray diffraction, X-ray photoelectron spectroscopy, nitrogen adsorption/desorption method and scanning electron microscopy. The charge storage properties of materials have also been investigated in three- and two-electrode configurations by means of cyclic voltammetry and galvanostatic charging/discharging in alkaline media. The results are consistent with the view that, depending on a method of preparation, the resulting nickel oxide films may exhibit redox characteristics different from that typically observed for nickel oxide-based materials. It is demonstrated that faradaic-type (redox) reactions, that are typical for battery-like materials, contribute predominantly to the high electrode capacity of  $257\text{C g}^{-1}$  (at  $0.1\text{ A g}^{-1}$ ). By combining nickel oxide with a capacitive material such as activated carbon within the two-electrode symmetric cell, systems with increased charge-storage capabilities have been obtained. The fact, that the voltage window of nickel oxide-based cell has been broadened positively from 0.6 V to 1 V upon introduction of activated carbon, has also resulted in the increase of the cell's energy and power densities as well.

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## 1. Introduction

Over the last few decades there has been growing interest in the development of new materials for various types of energy storage devices including electrochemical capacitors (supercapacitors) and secondary batteries [1,2]. The main advantages of supercapacitors over other charge storage systems are their high power density and almost unlimited durability. For example, activated carbons and carbon nanotubes are capable of storing energy mainly according to the double layer charging mechanism [1–3]. The systems are characterized by extremely fast charging/discharging rates resulting in high power capabilities. However, energy densities (expressed per mass or volume of carbon nanostructures) are still much lower than those offered by lithium-ion or even nickel-hydride batteries. Therefore, contributions originating from redox activities of the oxygen or nitrogen surface groups (on carbons) have also been considered [4,5].

Another approach refers the application of redox-active materials, for instance, hydrated ruthenium oxide ( $\text{RuO}_2$ ) [2,6–8]. However, because of high cost of ruthenium and its compounds, many recent studies have focused on non-noble transition metal oxides and conductive polymers [9–15]. In particular, nickel oxide ( $\text{NiO}$ ) and nickel hydroxide ( $\text{Ni}(\text{OH})_2$ ), similar to those used in Ni-Cd batteries, have been broadly investigated as relatively inexpensive, non-toxic and promising electroactive materials. There have been many papers describing nickel oxide and its derivatives as pseudocapacitive-type materials. However, when taking into account the fundamental definition of capacitance [1], the term pseudocapacitance should be used [16] only for the materials having the electrochemical signatures of the capacitive-type electrodes, i.e. characterized by linear dependencies of charge accumulated within certain ranges of applied potentials and the linear (mirror-like) galvanostatic charge-discharge responses [15]. Having in mind this definition, nickel oxide (undergoing charging-discharging according to a Faradaic mechanism) should be considered more as high-power battery-type rather than pseudocapacitive material.

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The interest in NiO-based materials of defined morphology and electrochemical identity has been intensively growing in the past few years [17–24]. The beneficial effect of introducing nanostructured carbons, providing electronically conductive carriers within the fairly resistive nickel oxides, should also be mentioned here [25–28]. The resulting systems have been typically diagnosed by monitoring the performance of a single-electrode in the three-electrode configuration rather than with use of more practical two-electrode systems. Alternatively, they have been considered as positive electrodes of asymmetric supercapacitors [28,29]. To our best knowledge, there are only a few reports showing utility of composites of nickel oxide with activated carbons relative to pristine NiO, in which “real” diagnostic systems such as symmetric two-electrode cells [30,31] have been applied.

In the present work, we demonstrate that the NiO material is capable of undergoing two redox processes, rather than to exhibiting a typical single ( $\text{Ni}^{\text{II/III}}$ ) redox transition, as typically observed. To fabricate NiO structures, we have modified a common synthetic procedure [30] by decreasing the precipitation temperature. This research parallels analogous recent attempts with nickel compounds [32]. We address here advantages and limitations of both pristine NiO and NiO supported onto activated carbon (AC), abbreviated as NiO/AC, exhibiting high gravimetric capacity up to  $257\text{C g}^{-1}$ . As a rule, the systems have been characterized using two-electrode symmetric cells. By introducing an additional electrode acting as the reference system, we have also been able to perform extra diagnostic experiments (e.g. permitting determination of potential windows of the cell electrodes). Special attention has been paid to the influence of ACs on the overall performance of symmetric NiO/AC-based cells. The energy and power densities as well as the operating voltage ranges are also compared and discussed.

## 2. Experimental

All solutions were prepared using double-distilled and deionized water. To produce a typical NiO precipitate,  $0.5\text{ mol dm}^{-3}$  NaOH solution was added dropwise into  $0.2\text{ mol dm}^{-3}$  Ni ( $\text{NO}_3$ )<sub>2</sub>·6H<sub>2</sub>O (Aldrich) under vigorous stirring. The solution was kept at pH = 8. The synthesized nickel hydroxide product was separated by centrifuging and washing with water and ethanol. Thus prepared samples were dried overnight at  $45^\circ\text{C}$  in air atmosphere.

To prepare activated-carbon-supported nickel-oxide (NiO/AC) composites (at the mass ratio of Ni to AC equal to 2.35), at first, 500 mg of AC (Norit<sup>®</sup> SX ULTRA, from Aldrich) was dispersed within  $0.1\text{ dm}^3$  of  $0.2\text{ mol dm}^{-3}$  Ni( $\text{NO}_3$ )<sub>2</sub>·6H<sub>2</sub>O solution using an ultrasound bath. Further steps were identical to those described above.

The powders of NiO and its composites with AC were finally obtained by annealing the as-prepared samples at  $250^\circ\text{C}$  for 4 h. Following the calcination steps, their color changed from light green to dark (almost black) what was consistent with the transformation of Ni(OH)<sub>2</sub> into NiO.

### 2.1. Structural and electrochemical characterization

Materials were examined using X-Ray diffraction (XRD) instrumentation equipped with Cu K-alpha radiation (Siemens D5000). The X-ray photoelectron spectroscopy (XPS) measurements were performed using PHI 5500 Spectrometer with monochromatic Al K $\alpha$  radiation (1487 eV). Nickel and oxygen spectra were energy-calibrated on the basis of the hydrocarbon peak with the binding energy of 285 eV. The specific surface area of the active materials was determined using the Brunauer-Emmett-Teller (BET) method at 77 K in N<sub>2</sub> (Belsorp Mini II). The pore size

distribution was calculated from the desorption branches of the isotherms via the Battreth-Joyner-Halenda (BJH) method. Surface morphology was achieved using scanning electron microscopy (ZEISS, Germany).

Electrochemical (cyclic voltammetric and galvanostatic charging–discharging) experiments were carried out using Autolab potentiostat PGSTAT 100. The working electrodes were prepared by brushing an ink-type suspension containing NiO or NiO/AC onto nickel foil current collectors (Goodfellow, 99.0% purity) of 10 mm diameters, followed by subjecting them to drying overnight at  $70^\circ\text{C}$ . The ink suspension was generated by dispersing the active material (75 wt%), acetylene black (15 wt%) and polyvinylidene difluoride (PVDF) (10 wt%) within N-methylpyrrolidone (NMP). The mass of the electroactive material for each electrode was equal to ca. 2.5 mg.

All of the electrochemical experiments were performed using Swagelok<sup>®</sup> cell with three-way valves. In the diagnostic three-electrode measurements, a nickel foil (modified with active material), carbon paper (thickness,  $190\text{ }\mu\text{m}$ ; Toray, Electrochem. Inc., USA), and the Ag/AgCl ( $3\text{ mol dm}^{-3}$  NaCl) electrode ( $E = 0.21\text{ V}$  vs. SHE) served as working, counter, and reference electrodes, respectively. The counter and working electrodes were assembled face to face, and separated by a glassy fibrous paper sheet (Whatman, GF/A). The reference electrode was inserted between the electrodes through a hole drilled in a one of Swagelok<sup>®</sup> cell valves.

To characterize electrochemical cells operating in two-electrode configuration, where the current imposed and the potential were recorded between the working (positive and negative) electrodes, the Ag/AgCl reference was also introduced to the cell to evaluate potential ranges of both electrodes (the data were simultaneously recorded by a LabJack U6 data acquisition device connected to a computer). The voltammetric and galvanostatic currents were expressed per average arithmetic mass of both electrodes (including binder and conductive agent).

## 3. Results and discussion

### 3.1. The physicochemical properties of active materials

The structure and composition of the synthesized NiO and NiO/AC materials were first evaluated by performing XRD measurements. It is apparent from Fig. 1(a) and (b) that the XRD pattern exhibits peak positions corresponding to (111), (200), (220), (311) and (222) planes characteristic of NiO (JCPDS card 00-047-1049,

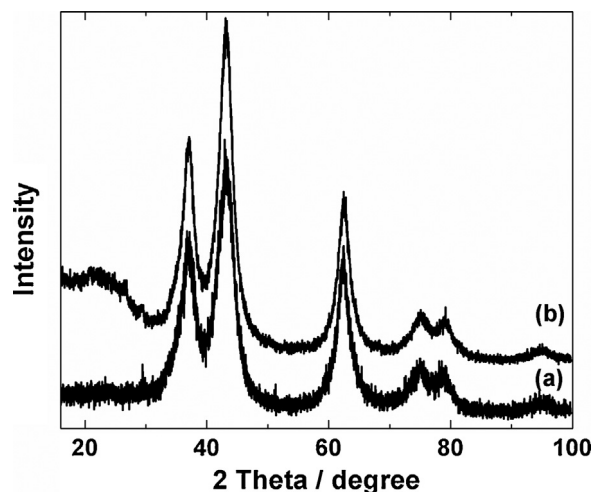


Fig. 1. XRD patterns of (a) NiO, and (b) NiO/AC composite.

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