Pseudocapacitance Properties of Co$_3$O$_4$ Nanoparticles Synthesized Using a Modified Sol-Gel Method

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This work reports the synthesis of nanoparticles cobalt oxide (Co$_3$O$_4$) with no secondary phase by a modified sol-gel method and its structural morphological and electrochemical characterizations. FTIR, XRD and Raman analysis showed the formation of spinel cobalt oxide with no secondary phase. TEM images revealed that an undefined morphology with average crystallite size estimated by Scherrer's equation was found to be 30 nm. Experiments of cyclic voltametric, galvanostatic charge-discharge and impedance spectroscopy were evaluated at 1 mol L$^{-1}$ KOH and revealed an intrinsic pseudocapacitance. The studies of complex capacitance and complex power revealed the resistive and capacitive characteristics with a specific capacitance of 120 F g$^{-1}$.

Keywords: Adapted Sol-gel Method, Co$_3$O$_4$ nanoparticles, pseudocapacitance, complex capacitance, complex power.

1. Introduction

Synthesis of nanoparticles semiconductor materials with different sizes and shapes are considered an attractive field of research. Physical and chemical properties such as high surface area, volume and high interfacial reactivity, make nanoparticles attractive in various fields of applications: catalysis, magnetic materials, sensors and energy storage like batteries and electrochemical capacitors. When the nanomaterial is used for the purpose of energy storage, it can be done in two ways, directly and indirectly. In the direct form, the materials are constituted with porous materials of large surface areas that allow the storage of electric charges by electrostatic adsorption on the surface and pores. In an indirect way, the material storage by quick faradaic reactions at the electrode/electrolyte interface by a mechanism known as pseudocapacitance. Indirect storage is possible in materials such as conductive polymers and oxides of transition metals. In metallic oxides, the pseudocapacitance can be classified as intrinsic or extrinsic. Intrinsic pseudocapacitance can charge storage for a wide range of particle sizes and morphologies. The main oxides studied are RuO$_2$, MnO$_2$, NiO, Fe$_3$O$_4$ and Co$_3$O$_4$.

Cobalt oxide is a semiconductor p-type that can exist in three different forms (CoO, Co$_2$O$_3$ and Co$_3$O$_4$), is naturally abundant and environmentally safe besides excellent redox activity and low cost compared to other transition metal oxides, such as ruthenium. Particularly as electrodes, in Co$_3$O$_4$ (cobaltosic oxide) form, cobalt oxide exhibits good electrochemical performance in alkaline solution, and faradaic redox processes occurring at the surface can be described according to the reactions $^{19}$ 1 and 2:

$$C_{Co}O_4 + OH^- + H_2O \rightleftharpoons 3C_{Co}OOH + e^- \quad 1$$

$$C_{Co} OOHI + OH^- \rightleftharpoons C_{Co}O_3 + H_2O + e^- \quad 2$$

Controlled synthesis of Co$_3$O$_4$ nanostructures applied on pseudocapacitive energy storage are studied by different synthesis methodologies. For instance, Shinde et.al. prepared Co$_3$O$_4$ thin films by the spray pyrolysis technique and obtained a specific capacitance of 74 F g$^{-1}$. By the microwave method Yan et.al. prepared a composite of Co$_3$O$_4$ and graphene nanosheet (GNS)/Co$_3$O$_4$ that presented a specific capacitance of 243 F g$^{-1}$. Using a hydrothermal method Wang et.al. obtained Co$_3$O$_4$ nanorods with a value of 280 F g$^{-1}$. Plasma spray route was used for Tummala et.al. to obtain electrodes films with specific capacitance of 166 F g$^{-1}$. The conventional sol-gel method has some advantages like high purity and form homogeneous
products with different morphologies and has been employed in obtaining nanostructures of oxides for the purpose of energy storage\(^{28,29,30}\). On the other hand, it uses organic solvents, expensive reagents and the control of pH and temperature are also necessary and generally more than one phase of cobalt oxide is produced together\(^{31,32,33}\). This work reports the synthesis of Co\(_3\)O\(_4\) nanopowder by an adapted sol-gel method, previously published by our research group\(^3\). The oxide obtained was characterized physically by techniques of infrared spectroscopy, X-ray diffraction, Raman spectroscopy and transmission electron microscopy. The electrochemical characterization was used to evaluate the capacitive characteristics of the energy storage through techniques of the cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy in KOH electrolyte that was studied for the concentration of 1 mol L\(^{-1}\).

2. Experimental

Poly(vinyl alcohol) (PVA, 87 - 89 wt.%) hydrolyzed and MW 146,000 - 186,000 were purchased from Aldrich. Co(NO\(_3\))\(_2\)\(\cdot\)6H\(_2\)O (98 wt.% Synth). The cobalt oxide nanoparticles were synthesized by an adapted sol-gel method. Aqueous diluted PVA (10% w/v) and saturated metal nitrate solutions were prepared separately and then mixed at Co\(^{2+}\): PVA monomeric unit ratio of 1:6. The solution was kept at room temperature under stirring for 2 h and then heated under vigorous stirring (approximately 250 °C), until total water evaporation and partial thermal degradation of the polymer. The nanoparticles material was achieved after calcination of the obtained powder under atmospheric air at 400 °C.

The cobalt oxide powder was characterized by infrared spectroscopy (FTIR) using FTIR-BOMEM-100 Spectrometer with KBr pellet. The crystalline phase was identified by X-ray diffraction (XRD) using Shimadzu XRD-6000X-ray diffractometer with monochromated Cu-K\(_\alpha\) radiation (\(\lambda = 1.5406 \) Å). Reflection X-ray powder diffraction data were obtained in the following conditions: 2\(\theta\) = 10 - 80°, 40 kV, 30 mA, scan rate of 2 min\(^{-1}\) and slit width of 0.30 mm.

Raman measurement was carried out using Bruker Senterra Raman microscope with 785 nm laser radiation and laser power of 25 mW. The spectra were acquired by averaging hundred acquisitions of 3 s with a \(\times 20\) objective. The obtained cobalt oxide morphology was analyzed using 120 kV JEOL JEM-1400 transmission electron microscope (TEM) with a Carl Zeiss EM10 microscope operating at 80 KV.

Cyclic voltammograms, chronoamperometric and electrochemical impedance experiments were carried out in a conventional three-electrode cell using Autolab Potentiostat (PGSTAT 302N). The cobalt oxide powder prepared by a homogeneous mixture of Co\(_3\)O\(_4\) nanoparticles (85 wt%), activated carbon (10 wt%) and polytetrafluorethylene (PTFE, 5 wt%)\(^{35}\) was deposited onto a titanium substrate and used as working electrode. Ag/AgCl/saturated KCl electrode was used as a reference electrode and a KOH solution as electrolyte. Cyclic voltammograms were recorded at scan rates of 1, 10 and 25 mV s\(^{-1}\) in the potential range of 0 - 0.6 V, at room temperature. Charge/discharge tests were recorded for current densities of 1, 3 and 5 mA cm\(^{-2}\) in the same potential range of voltammograms. Electrochemical impedance measurements were conducted in 0.4 V with the aid of a frequency response analyzer module coupled to the model AUTOLAB FRA. After 300 s polarization, spectra were obtained in the frequency range of 10 mHz to 10 kHz, to which an alternating disturbance 10mV peak to peak was applied.

3. Results and Discussion

The cobalt oxide as obtained was analyzed by FTIR spectroscopy and its spectrum is depicted in Fig. 1a. Two absorption bands centered at 651 cm\(^{-1}\) and 565 cm\(^{-1}\) are assigned to the fingerprint stretching vibrations of Co-O bond\(^{36}\). The band at 565 cm\(^{-1}\) is related to Co-O vibrations in the octahedral site, whereas the band at 651 cm\(^{-1}\) is associated to Co-O vibrations in the tetrahedral site of the lattice, indicating the formation of pure phase of Co\(_3\)O\(_4\)\(^{17}\). The presence of these bands in the lower wavenumber region suggests that the materials were finely crystallized in the nano range\(^{38}\).

X-ray diffraction pattern of cobalt oxide nanoparticles produced with refinement by the Rietveld method performed using the GSAS-EXPGUI software package is presented in Fig. 1b. And it is possible to see peaks at \(\approx 19°, 32°, 36°, 39°, 45°, 56°, 59°, 66°, 74°, 77°\) and 78° referent to (111), (220), (311), (222), (400), (422), (333), (440), (620), (533) and (622) planes, corresponding to Co\(_3\)O\(_4\). The obtained lattice parameters, with Rietveld method, were \(a = b = c = 0.8091\) nm, with a satisfactory agreement with ICSD # 9362 (\(a = b = c = 0.8065\) nm)\(^{39}\), corresponding to a single phase of spinel structure, indicating nanoparticles in the Co\(_3\)O\(_4\) compound. The average size of crystallitles calculated by Scherrer's equation was obtained with approximately 30 nm, caused by the reduced crystallite size and the crystalline lattice distortion. All the diffraction peaks could be well indexed to spinel Co\(_3\)O\(_4\) phase (JCPDS 42-1467).

Raman spectrum of the synthesized nanoparticle material is depicted in Fig. 1c. It has clearly displayed five well-defined peaks located at approximately 194, 478, 518, 616 and 686 cm\(^{-1}\), which correspond, respectively to the \(A_{ig}\), \(F_2\)'s, \(F'_2\)'s, \(E\) and \(F_4\)'s modes of Co\(_3\)O\(_4\) crystalline, in agreement with the group theory\(^{40}\). When compared with the Raman-active phonon modes of Co\(_3\)O\(_4\), these peaks show a red-shift\(^{41}\). This phenomenon is attributed to the optical phonon confinement effect in nanoparticles that can cause uncertainty in the phonon wave vectors and then a downshift of the Raman peaks\(^{42}\). These results are consistent with the result of Co\(_3\)O\(_4\) nanoparticles for XRD.
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Figure 1. (a) FTIR spectrum of the synthesized Co$_3$O$_4$ nanoparticles. (b) XRD pattern for Co$_3$O$_4$ nanoparticles: simulation (Rietveld), experimental and residual lines (difference between experimental and simulated patterns). (c) Raman spectrum of Co$_3$O$_4$ nanoparticles. (d) TEM image of the Co$_3$O$_4$ nanoparticles

Fig. 1d shows a representative TEM image taken from Co$_3$O$_4$ nanoparticles. The image reveals undefined shape with similar particle size forming agglomerates that can be associated with the high surface energy of the nanometric crystals. The material synthesized when compared to other sol-gel methods, we can observe that the size of particles and agglomerates are similar, around 10 and 20 nm$^{26,43}$. The voltammograms for the Co$_3$O$_4$ electrode at scan rates of 1, 25 and 100 mV s$^{-1}$ in the potential range of 0 - 0.6 V for 1 mol L$^{-1}$ KOH electrolyte is shown in Fig. 2a. It must be noted that the shapes of the curves are different from the shape presented by the electrical double layer capacitor which has closed rectangular shape and stored energy through non-faradaic processes$^{44}$. The voltammograms show forms that are typical of the materials that are strongly governed by faradaic processes with defined distinct anodic and cathodic peaks that represent the oxidation and reduction reactions occurring on the surface of Co$_3$O$_4$ electrode. The shape of the curves and the positions of the peaks (oxidation and reduction) in the voltammograms varied as a function of scan rate. The increase of scan rate caused a decrease in the definition and a displacement of those peaks. According to Zhang$^{41}$ the anodic peaks appear in the potential range of 0.4 to 0.6 V and represent the oxidation reactions of Co$_3$O$_4$ to CoOOH and CoOOH to CoO$_2$. The cathodic peaks appear in the potential range of 0.3 to 0.5 V and represent the reduction reactions of Co$_3$O$_4$ to CoOOH and CoOOH to Co$_3$O$_4$ that are occurring on the surface of the electrode. To 25 mV s$^{-1}$ scan rate the oxidation peak with a maximum at 0.55 V was broadest than the scan rate 1 mV s$^{-1}$, that was near 0.5 V. This suggests that a portion of material is not accessible when there is an increase of the scan rate, while lowest scan rate allows electrochemistry adsorption/desorption of the OH$^-$ ions in the outer surface and inside the pores. On the other hand, the increase of scan rate allows access ions only on the external surface and, in this case, decreasing the storage charge values. According to Tummala$^{22}$ the displacement of oxidation peaks to higher potentials and reduction peaks for lower potential may be related to conductivity and to the polarization of the electrode.

Fig. 2b shows the charge-discharge curves for current densities of 1, 3 and 5 mA cm$^{-2}$, at a potential range of 0 to 0.6 V in 1 mol L$^{-1}$ KOH. In general, the shapes of the curves did not present good symmetry between the charge-discharge
Figure 2. (a) Cyclic voltammograms at 1, 10 and 25 mV s\(^{-1}\) and (b) Charge-discharge at 1, 3 and 5 mA cm\(^{-2}\) at 1 mol L\(^{-1}\) of KOH for the Co\(_3\)O\(_4\) nanoparticles

processes, and the curves were not ideally linear. A good symmetry may be related to a good reversibility of loading and unloading processes\(^{46}\) and according to Vijayakumar\(^{14}\) nonlinearity is a confirmation of the pseudo-capacitive nature of the electrode. Discharge curves showed two distinct parts. Initially, the discharge curves show a resistive component which is represented by a rapid ohmic drop at the beginning of the discharge curve, it represents an internal resistance\(^{46}\) and a capacitive part, represented by a potential decay over time at different inclinations due to Faradaic processes occurring in electrode surface\(^{47}\). According to Lee\(^{48}\) the rapid ohmic drop in potential is a characteristic of electrodes constituted by oxides of transition metals. The curves show that the increased current density favored the increase of the internal resistance. At low current density, the internal resistance is lower and allows a greater number of active sites utilized, which contributes to a higher stored energy.

The Nyquist plot, Fig. 3a, for the Co\(_3\)O\(_4\), and it is noted that high frequencies, where the curve intersects the real axis (axis \(Z'\)), have the electrolyte resistance (\(R_s\)) present values close to 0.4 \(\Omega\). The semicircle in the high frequency region corresponds to the charge transfer resistance (\(R_{ct}\)) due to faradaic reactions occurring at the electrode surface. The value \(R_{ct}\) to Co\(_3\)O\(_4\) electrode is 3.6 \(\Omega\).

The imaginary part of the complex impedance \(Z''\) in the region of least frequency provides information about the diffusive and capacitive processes. The straight line slope in the low frequency region for value close to 90\(^\circ\) with respect to the axis \(Z'\) suggests that the capacitive behavior of Co\(_3\)O\(_4\) electrode is not controlled by diffusion processes\(^{49}\). The capacitive behavior was studied by the equation\(^{50}\):

\[
C'(\omega) = \frac{1}{m \omega Z''(\omega)}
\]

where \(\omega = 2\pi f\) is the angular frequency of the applied alternating current (ac) signal, \(m\) is the mass and \(Z''\) is the imaginary part of the impedance. The behavior of capacitance values with frequency from equation 1 is shown in Figure 3b. It was verified that for lowest frequency the capacitance maximum values obtained were of 120 F g\(^{-1}\).

The data of electrochemical impedance spectroscopy were used at the study of complex capacitance to get the information of the relaxation time constant \(T_0\) that represents the transition from resistive to the capacitive behavior\(^{51}\). The complex capacitance is expressed by the equation\(^{52,53}\):

\[
C'(\omega) = C'(\omega) - jC''(\omega)
\]

where \(j\) is imaginary number while the angular frequency is \(\omega\). \(C'(\omega)\) e \(C''(\omega)\) are the real and imaginary part of the complex capacitance \(C(\omega)\) calculated by the following equations:

\[
C'(\omega) = \frac{-z''(\omega)}{\omega |Z(\omega)|^2}
\]

\[
C''(\omega) = \frac{z'(\omega)}{\omega |Z(\omega)|^2}
\]

where \(|Z(\omega)|\) is the module of the complex impedance calculated by \(Z(\omega)=Z'(\omega)-jZ''(\omega)\).

Figure 3c shows the imaginary part of the complex capacitance \(C''(\omega)\) as a function of frequency for the studied concentration. The information of the relaxation time constant \(T_0=f_{c}^{-1}\) was obtained by a maximum in frequency in \(f_c\). For frequencies \(f > f_c\) the electrode presents the behavior of the resistor and for frequencies \(f < f_c\) the electrode presents the behavior of the capacitor. Material that presents small values for the relaxation time constant exhibits rapid power delivery and provide high power density\(^{54}\). The Co\(_3\)O\(_4\) electrode presented a relaxation time constant about 20 s. Considering the frequency range used, the relaxation time constant varies from 0 to 100 s. The value obtained shows that during 20 s the electrode presented the behavior of the resistor and the time remaining presented the behavior of the capacitor.
Another form to express the data of electrochemical impedance is the study of complex power that shows the behavior of the active power (dissipated power) and reactive power (capacitive power) with the frequency. The total energy in circuits of alternating perturbation is the sum of the energy stored and the energy transferred in one direction. The total power \( S \) associated with this energy can be expressed in the complex form as the sum of the real part, transferred power or active power \( P \), and the imaginary part, stored power or reactive power \( Q \), as follows\(^5\):

\[
S(\omega) = P(\omega) + jQ(\omega)
\]

where \( P \) is the active power and \( Q \) is the reactive power calculated by relations

\[
P(\omega) = \omega C^\prime(\omega)|\Delta V_{\text{rms}}| \tag{6}
\]

\[
Q(\omega) = \omega C^\prime(\omega)|\Delta V_{\text{rms}}| \tag{7}
\]

where \( \Delta V_{\text{rms}} = \Delta V_{\text{max}}/\sqrt{2} \) and \( \Delta V_{\text{max}} \) is the maximum amplitude of the applied ac perturbation.

The power dissipated was analyzed from the normalization of the active and reactive powers, \(|P|/|S|\) and \(|Q|/|S|\), respectively. When the normalized powers \(|P|/|S|\) and \(|Q|/|S|\) are on the same graph as a function of frequency (Fig. 3d) it is verified that the concentrations studied began to present a capacitive response for frequency below 10 Hz and below 0.1 Hz showed a predominant capacitive behavior.

The set of the electrochemical tests indicate an intrinsic pseudocapacitance. The technique of cyclic voltammetry presented a curve with wide peaks and small peak-to-peak voltage separation (oxidation and reduction). The galvanostatic charge-discharge presented a curve with intermediate form of the forms presented by the materials used in batteries and capacitors. The impedance spectroscopy presented a curve containing a semicircle at high frequency followed by a straight line with a slope close to 90°\(^10,56\).
4. Conclusion

Coastal oxide nanoparticles $\text{Co}_3\text{O}_4$ were successfully prepared with an adapted sol-gel method. TEM images exhibit that the synthesized nanomaterial has no defined morphology. FTIR and DRX show the formation of nanoparticles $\text{Co}_3\text{O}_4$ spinel without the presence of secondary phases with the average size of the crystallites with about 30 nm. Raman Spectroscopy results confirm that observed peaks are characteristics of crystalline modes and consistent with the group theory for $\text{Co}_3\text{O}_4$. The electrochemical tests revealed the characteristics of the resistive and capacitive behavior, showed an intrinsic pseudocapitance with specific capacitance of 120 F g$^{-1}$, which indicates that the method may be an option to obtain the cobalt oxide $\text{Co}_3\text{O}_4$ applied in the energy storage.

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6. References


