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Sustainable synthesis of cobalt nanoparticles for supercapacitor application

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Abstract: The growing demand for renewable energy sources and the continuous increase in global energy demand are responsible for the need to develop new forms of energy storage. In this context, supercapacitors emerged due to properties, such as high charge density, long durability and reduced environmental impact. This work aims to develop electrodes based on cobalt oxide synthesized by ionizing radiation for use in supercapacitors. Synthesis by ionizing radiation consists of a sustainable and ecological approach to the production of nanoparticles, reducing the need for toxic reagents and high temperatures. Cobalt oxide nanoparticles were synthesized by irradiating a solution of cobalt acetate, followed by vacuum filtration and drying. The electrochemical properties of the material were evaluated using cyclic voltammetry in 1 M KOH. The results indicated that the cobalt oxide electrodes have a significant energy storage capacity, indicating their potential for use in supercapacitors.

Keywords: sustainable, synthesis, radiation, supercapacitors.

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Síntese sustentável de nanopartículas de cobalto para aplicação em supercapacitores

Resumo: A crescente demanda por fontes renováveis de energia e o contínuo aumento do consumo global de energia são responsáveis pela necessidade de desenvolver novas formas de armazenamento de energia. Neste contexto, os supercapacitores destacam-se por suas qualidades, como alta densidade de carga, longa durabilidade e impacto ambiental reduzido. Este trabalho busca desenvolver eletrodos baseados em óxido de cobalto sintetizado por radiação ionizante para uso em supercapacitores. A síntese por radiação ionizante representa uma abordagem sustentável e ecológica para a produção de nanopartículas, reduzindo a necessidade de reagentes tóxicos e altas temperaturas. As nanopartículas de óxido de cobalto foram sintetizadas através da irradiação de uma solução de acetato de cobalto, seguido pela filtração a vácuo e secagem. As características eletroquímicas do material foram avaliadas através de voltametrias cíclicas em KOH 1 M. Os resultados indicaram que os eletrodos de óxido de cobalto têm uma capacidade significativa de armazenamento de energia, corroborando seu potencial para uso em supercapacitores.

Palavras-chave: sustentável, síntese, radiação, supercapacitores.

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1. INTRODUCTION

With the increasing demand for the replacement of fossil energy sources with renewables, together with the growth in global energy consumption, new challenges arise in enhancing the efficiency of these energy systems and mitigating the direct and indirect impacts of their implementation. A crucial aspect that significantly influences the efficiency of these systems is the effectiveness of energy storage systems [1].

Various types of supercapacitors, considered promising energy storage systems, have been developed in recent years. These devices offer significant advantages over conventional batteries, such as higher power density, extended lifespan, and lower environmental impact. Given these characteristics, numerous studies have been conducted to enhance the efficiency of these devices [2].

The active material used in the production of supercapacitor electrodes is one of the most critical factors in achieving high performance. Transition metal oxides have been receiving a lot of attention due to its high theoretical specific capacitance [3].

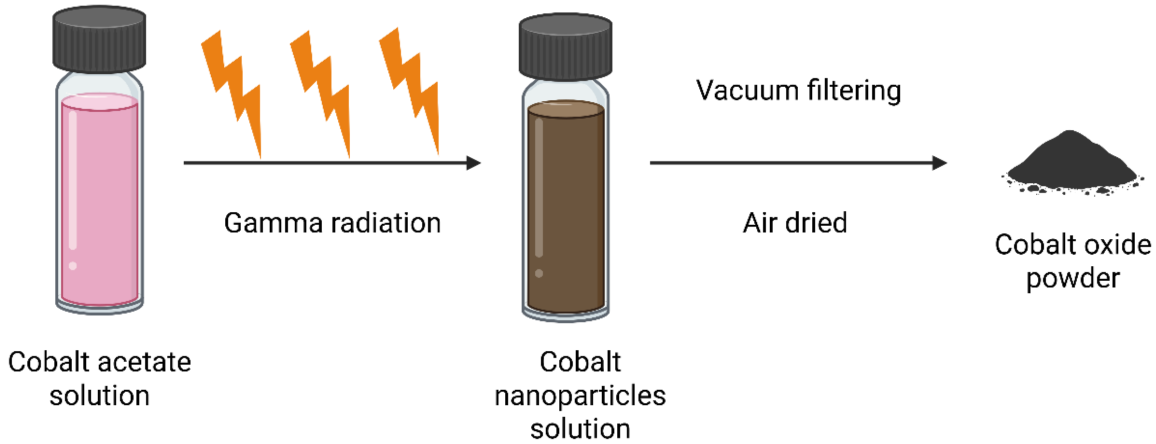
Many techniques for producing nanoparticles use toxic chemical reductants, require long reaction times or involve high-temperature treatments [4],[5]. In contrast, gamma radiation synthesis offers an appealing alternative for fabrication due to its environmentally friendly characteristics [6]. Synthesis by ionizing radiation operates at room temperature in an aqueous solution, reducing the need for toxic reagents or the production of unwanted by-products [7].

This study aims the development of electrodes based on cobalt oxide nanoparticles, produced through an environmentally friendly process using gamma radiation, for supercapacitors application.

2. MATERIALS AND METHODS

The cobalt oxide nanoparticles were prepared by mixing cobalt acetate tetrahydrate (0.1 M, >98%, Sigma-Aldrich) in ultrapure water in glass vials and irradiating with gamma radiation at 50 kGy. After irradiation, the dispersions were vacuum filtered using polytetrafluoroethylene filter paper (0.2 µm, Sartorius Stedim Biotech GmbH) and air-dried.

Figure 1: Schematic of cobalt nanoparticle synthesis.



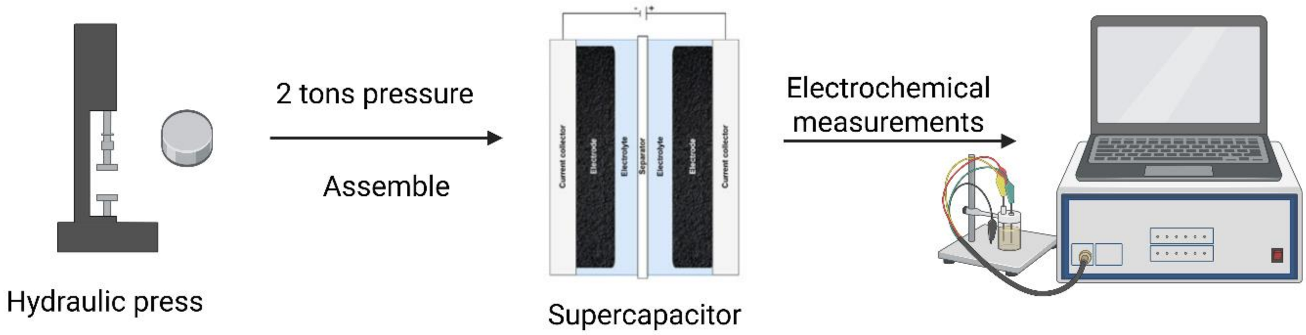
Source: Author using BioRender.

X-ray diffraction (XRD) measurements were performed on a X-ray diffraction from Rigaku, model SmartLab SE available at the Nuclear Reactor Center (CERPq-IPEN/CNEN-SP), equipped with copper tube and scintillation detector, with counting times of 6 seconds per step size of 0.1º.

The cobalt oxide electrode was fabricated using 56.7% cobalt oxide, 7.1% Vulcan carbon, and 36.3% PTFE (polytetrafluoroethylene). The Vulcan carbon was first dispersed in isopropyl alcohol along with the PTFE to form a conductive binder. The active material was then added to the mixture, which was homogenized and dried in an oven at 80 ºC. After drying, the material was divided into two parts, which were pressed in a hydraulic press under 2 tons of pressure, as shown in figure 2.

The resulting electrodes were then assembled with a separator between two conductive graphite plates immersed in a 1 M KOH media, both electrodes act as a reference for each other, and the potentials are measured relative to the device itself. The cyclic voltammetry analyses were performed using a Princeton Applied Research potentiostat, model Versastat 4, with data acquisition and processing carried out through the VersaStudio software.

Figure 2: Schematic of electrochemical measurements.



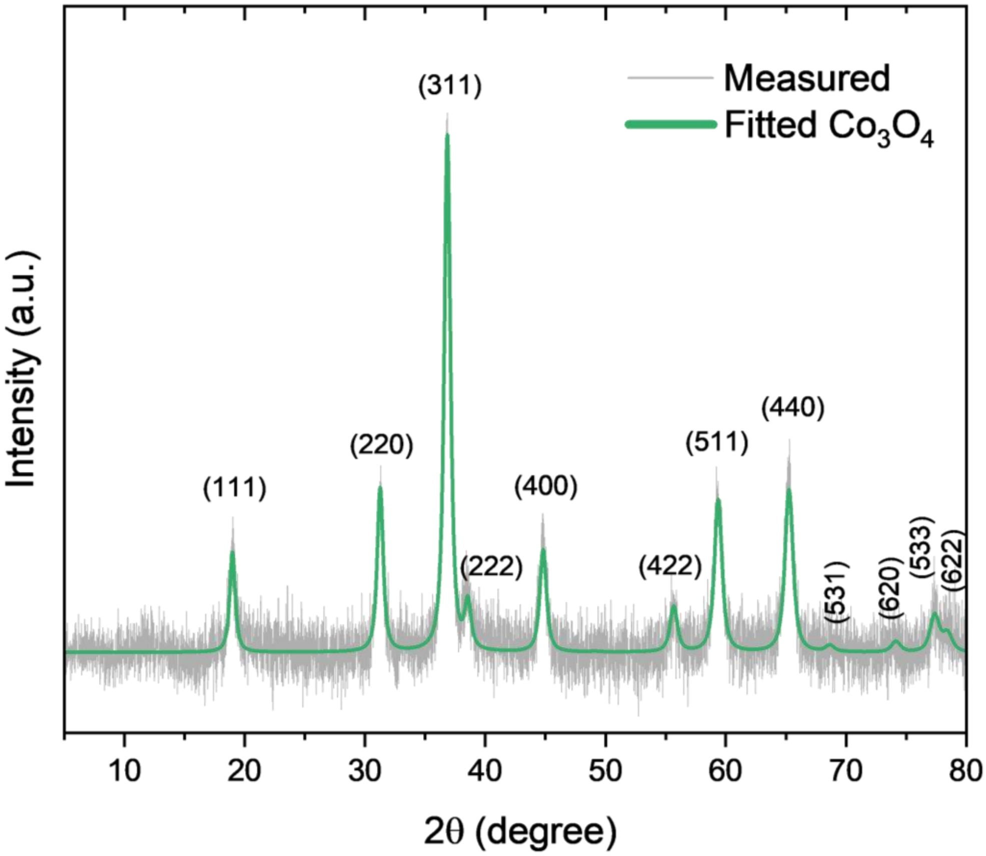
Source: Author using BioRender.

The Rietveld refinement of the XRD data was performed using Profex 5.3 [8]. Schematics were assembled with BioRender and graphics were built using Origin 2024.

3. RESULTS AND DISCUSSIONS

X-ray diffraction analysis was performed to evaluate the formation of the cobalt oxide and the characteristics of its crystalline structure. From the obtained diffractogram it was realized a Rietveld refinement, with the fitting for Co_3O_4 showed below.

Figure 3: Diffractogram obtained from the cobalt nanoparticles synthesized.



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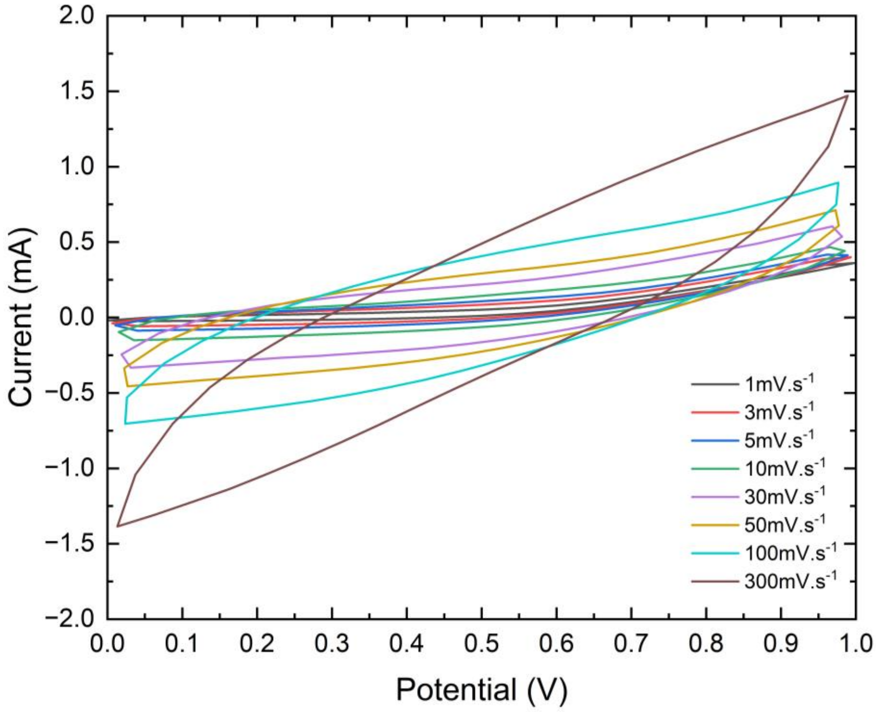
From the diffractogram, it was possible to detect peaks that can be perfectly indexed to the profiles of cubic spinel Co_3O_4 (JCPDS no. 43-1003) [7]. The peaks appeared at 19.0°, 31.3°; 36.9°, 38.6º, 44.8°, 55.7º, 59.4º, 65,3º 68,7º, 74.2º, 77.4º and 78.4° corresponding respectively to (111), (220), (311), (222), (400), (422), (511), (440), (531), (620), (533) and (622) crystal planes.

Also, we determined the lattice parameter of 8.09 Å and a crystallite size of 16.18 nm. It is noteworthy that the crystallite size does not correspond to the size of a nanoparticle and that this value does not reflect the real size of our nanomaterial. The data obtained, together with corresponding literature data, confirmed the successful synthesis of Co_3O_4.

To the electrochemical evaluation of the synthesized material, the cyclic voltammetry tests were conducted over a potential range from 0.0 V to 1.0 V, using scan rates of 1, 3, 5, 10, 30, 50, 100, and 300 mV/s. The obtained voltammograms are shown below.

Figure 4: Cyclic voltammograms obtained for 1M KOH in different scan rates.



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The patterns of the voltammograms obtained were consistent with those expected for supercapacitors, indicating that the electrode produced with the synthesized material exhibited the anticipated properties of supercapacitor materials.

For the calculation of the specific capacitance of the electrode it was used the following general equation [10]:

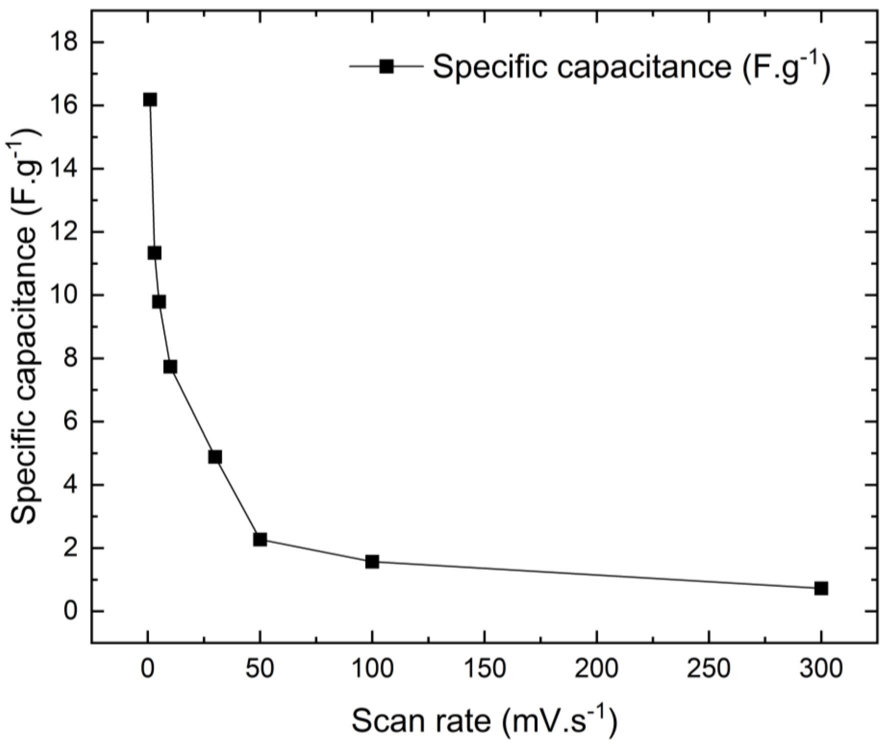
$$C = \frac{\int_{V_i}^{V_f} i(V)dV}{2\nu\,(V_f - V_i)}$$

In this equation, C represents the specific capacitance, m indicates the mass of the active material (in grams), V_f - V_i denotes the potential window (in volts), ν represents the scan rate (in volts per second), and I (V) refer to the current response at a given potential.

Table 1: Calculated specific capacitance for different scan rates.

SCAN RATE ($mV.s^{-1}$)	SPECIFIC CAPACITANCE ($F.g^{-1}$)
1	16.19
3	11.34
5	9.79
10	7.74
30	4.89
50	2.27
100	1.57
300	0.73

Figure 5: Plot of the specific capacitance curves calculated for various scan rates.



Source: Author.

From the specifically calculated capacitances, it was possible to notice the material capacity to store energy. However, comparing it with supercapacitors of cobalt oxide nanoparticles it was noticed that the capacitance obtained by our measurements were at least ten times lower than the reported previously by literature [3], [5], [9]. This could be related to an eventual lower surface area of our synthesized material, due to characteristic aggregation of Co_3O_4 nanoparticles and the influence of surface area for electrochemistry performance.

4. CONCLUSIONS

Based on the results obtained, it was possible to confirm the successful synthesis of the material using a green and more sustainable approach. The synthesized material's potential for electrochemical applications was also evaluated through cyclic voltammetry and also the capacity of energy storage. Additionally, conducting further electrochemical measurements, including galvanostatic charge-discharge and electrochemical impedance spectroscopy, to acquire comprehensive data on the electrochemical stability of the synthesized material and its energy storage mechanisms.

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CONFLICT OF INTEREST

All authors declare that they have no conflicts of interest.

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