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RESEARCH ARTICLE

ENHANCED SUPERCAPACITOR PERFORMANCE WITH NICKEL OXIDE AND ACTIVATED CARBON COMPOSITES IN WATER-IN-SALT ELECTROLYTE (WISE)

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Abstract. Supercapacitors are high-power density energy storage systems, yet increasing their energy density remains a key challenge. Activated carbon (AC) is a widely used electrode material in supercapacitor due to its high surface area, but its capacitance is often limited. In this work, integrating AC with nickel oxide (NiO), which offers a high theoretical capacitance of up to 2584 F g^{-1} has been explored to enhance charge storage and further boost energy density. The electrochemical performance of supercapacitors using NiO/AC composites with weight ratio (g/g) of 1:3 (NC513), 1:1 (NC511) and 3:1 (NC531) was investigated and compared to a pure AC electrode (NC50). NiO was synthesized via precipitation, calcined at 400 °C, and characterized using X-ray diffraction (XRD) and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX). Electrochemical testing was conducted using a three-electrode system for linear sweep voltammetry (LSV) analysis. A symmetrical two-electrode system was fabricated for cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) analysis in a water-in-salt electrolyte of 15 M $Ca(NO_3)_2$. All electrodes achieved a 2.5 V potential window, with electric double-layer capacitor (EDLC) behavior. SEM analysis reveals a fragmented structure and increased roughness on NC513, enhancing electrolyte accessibility. This explains NC513's optimized performance, with the highest specific capacitance of 35.32 F g^{-1} at 10 mV s^{-1} and an energy density of 9.96 Wh kg^{-1} at 0.5 A g^{-1}, with the lowest iR drop (0.1 V), outperforming NC50. These findings highlight the potential of optimized NiO/AC (NC513) composites for enhancing supercapacitor performance by improving charge storage capability and conductivity. This study advances safer, high-performance supercapacitors, offering valuable insights into electrode material design for next-generation energy storage.

Keywords: Nickel oxide, supercapacitor, water-in-salt.

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1. INTRODUCTION

The global energy storage market is projected to grow nearly fivefold, reaching USD 14.74 billion over the next decade, driven by the rapid adoption of renewable energy sources and the transition to sustainable energy solutions [1]. Supercapacitors (SCs) have gained significant attention due to their exceptional cycle life, rapid charge/discharge capabilities, and high specific power, making them suitable for applications ranging from backup power systems to portable electronics and electric vehicles [2]. Among SCs, electric double-layer capacitors (EDLCs) are the most widely studied, relying on a physical charge storage mechanism where energy is stored through reversible ion adsorption and desorption at the electrode-electrolyte interface [3].

Electrode material is crucial in defining the performance of EDLCs. Activated carbon (AC) is one of the most widely used electrode material for EDLCs due to its high surface area, excellent chemical stability, and cost-effectiveness, which contribute to superior power density [4]. However, to further enhance the energy storage capabilities, researchers have explored incorporating transition metal oxides (TMOs) as electrode materials, which provide additional capacitance through surface redox reactions. Among the TMOs studied, ruthenium oxide (RuO_2) stands out for its remarkable specific capacitance and conductivity, but its high cost limits its widespread application in SCs [5]. More affordable alternatives, such as manganese dioxide (MnO_2) and cobalt oxide (Co_3O_4) have been explored, but challenges remain regarding their conductivity and ion transport efficiency [6,7]. In this work, NiO has gained attention due to their high specific capacitance while also offering a unique combination of low cost and non-toxic properties [8].

Over the years, various strategies have been explored to further enhance the performance of EDLCs. One notable approach is the development of NiO/AC composite electrodes, which leverage the high surface area of AC and the Faradaic charge storage of NiO. These composites have demonstrated superior electrochemical performance compared to single metal oxide electrodes [9]. Studies by Yadav & Tripathi [10] and Lota et al. [11] show that NiO/AC electrodes achieve high capacitance, making NiO promising for symmetric supercapacitors in 6 M potassium hydroxide (KOH) electrolytes. However, KOH, an aqueous electrolyte constrained by its narrow electrochemical stability window (ESW) below 1.3 V [12]. For instance, Bulla et al. [8] reported an ESW of 1.2 V in a 2 M KOH system, while Yumak et al. [13] reported an ESW of 1.0 V in 6 M KOH.

To address this limitation, researchers have turned to water-in-salt electrolytes (WiSE), which provide a broader ESW of up to 3 V, while maintaining the inherent safety of aqueous systems, high ionic conductivity, and excellent ambient stability [14]. Previous studies have demonstrated the potential of WiSE formulations of sodium perchlorate ($NaClO_4$) and sodium nitrate ($NaNO_3$) in improving SCs performance [15,16]. Thareja and Kumar [15] reported that a 17 M $NaClO_4$ electrolyte achieved an ESW of 2.7 V with N-doped reduced graphene oxide electrodes. Guo et al. [16] found that 12 M $NaNO_3$ electrolyte reached 2.56 V ESW using commercial activated carbon (YP50F) electrodes. However, there are no studies that have yet investigated the use of WiSE with NiO/AC electrodes for supercapacitor applications.

In this study, a new WiSE electrolyte, 15 M calcium nitrate $Ca(NO_3)_2$, was selected for its high solubility, neutral in pH and low cost, making it a more economical and sustainable alternative to perchlorate and sulfate salts as WiSE [16]. This electrolyte achieves a potential window of up to 2.5 V with NiO/AC as electrode composite. This research focuses on optimizing the NiO/AC ratio to enhance supercapacitor performance. The findings provide valuable insights into determining the optimal NiO content required to achieve superior electrochemical performance.

2. MATERIALS AND METHODS

2.1 Synthesized NiO and Characterization

The synthesis of NiO was adapted from Yadav & Tripathi [10], using a precipitation method with precursor of nickel(II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) and sodium hydroxide (NaOH) as the precipitating agent. NiO was prepared under calcination temperature of 400 °C for 3 hours. The characteristics of the synthesized NiO powders were analyzed using SEM-EDX and XRD.

2.2 Electrode Fabrication

Carbon electrode fabrication was carried out following the method described by Farm [3] with minor modification. A mixture of activated carbon (YP50F), carbon black (C45), and Polyvinylidene fluoride (PVDF) as binder in a weight ratio of 8:1:1 was combined with N-methyl-2-pyrrolidone (NMP) solution to form a paste, which was evenly coated onto battery-grade aluminum foil (current collector) to a thickness of 100 µm and oven dried overnight. The dried electrode was then cut into 15 mm diameter discs for the preparation of coin cells. For carbon electrodes incorporating NiO, the NiO was synthesized in three different weight ratios NiO/AC (1:1 (50% NiO) - NC511, 1:3 (25% NiO) - NC513, and 3:1 (75% NiO) - NC513). The pure AC electrode was designated as NC50. C45 and PVDF/NMP were subsequently added to form a slurry, with the NiO/AC:CB:PVDF weight ratio set at 8:1:1.

2.3 Electrochemical Analysis

The electrochemical performance of the electrode was measured using a potentiostat/galvanostat (Autolab PGSTAT302). A three-electrode setup was employed to determine the potential window using linear sweep voltammetry (LSV), with the NiO/AC composite electrode as the working electrode, silver/silver chloride (Ag/AgCl) as the reference electrode, and platinum (Pt) strips as the counter electrode. Subsequently, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge-discharge (GCD) measurements were conducted using a symmetrical coin cell configuration. The specific capacitance, Cs (F g^{-1}), energy density, Ed (Wh kg^{-1}) and power density, Pd (W kg^{-1}) were calculated based on previously established equations [3,15]. $\int$ I(V) dV is area of CV curve, ΔV is the potential window (V), m is mass of active materials in both electrodes (g), S is scan rate (mV s^{-1}) and Δt is discharging time (s).

$$Cs = \frac{\int I(V)dV}{m \times \Delta V \times S} \quad (1)$$

$$Ed = \frac{1}{2} C_s \Delta V^2 \frac{1000}{3600} \quad (2)$$

$$Pd = \frac{E_d}{\Delta t} \times 3600 \quad (3)$$

3. RESULTS AND DISCUSSION

3.1 Surface Characterisation

The morphology of the synthesized sample calcined at 400 °C, as shown in Figure 1 (a), reveals micrometer-sized NiO particles with irregular shapes and a rough, fragmented surface. EDX analysis in Figure 1 (b) confirmed the composition of sample, with Ni (74.9 wt.%), O (20.1 wt.%), and C (5.0 wt.%), indicating successful NiO formation with minimal carbon contamination, likely from residual precursors. XRD in Figure 1 (c) further validated this, showing diffraction peaks at 2θ corresponding to the (111), (200), (220), (311), and (222) planes, which align with the standard face-centered cubic

(FCC) of NiO pattern (JCPDS 47-1049) and shows same peaks as previous studies by Yadav & Tripathi [10] and Lota et al. [11]. A minor peak at 2θ ≈ 26° suggests a trace of carbon presence, supporting the EDX results. The absence of unidentified peaks confirms the high purity of the synthesized NiO phase.

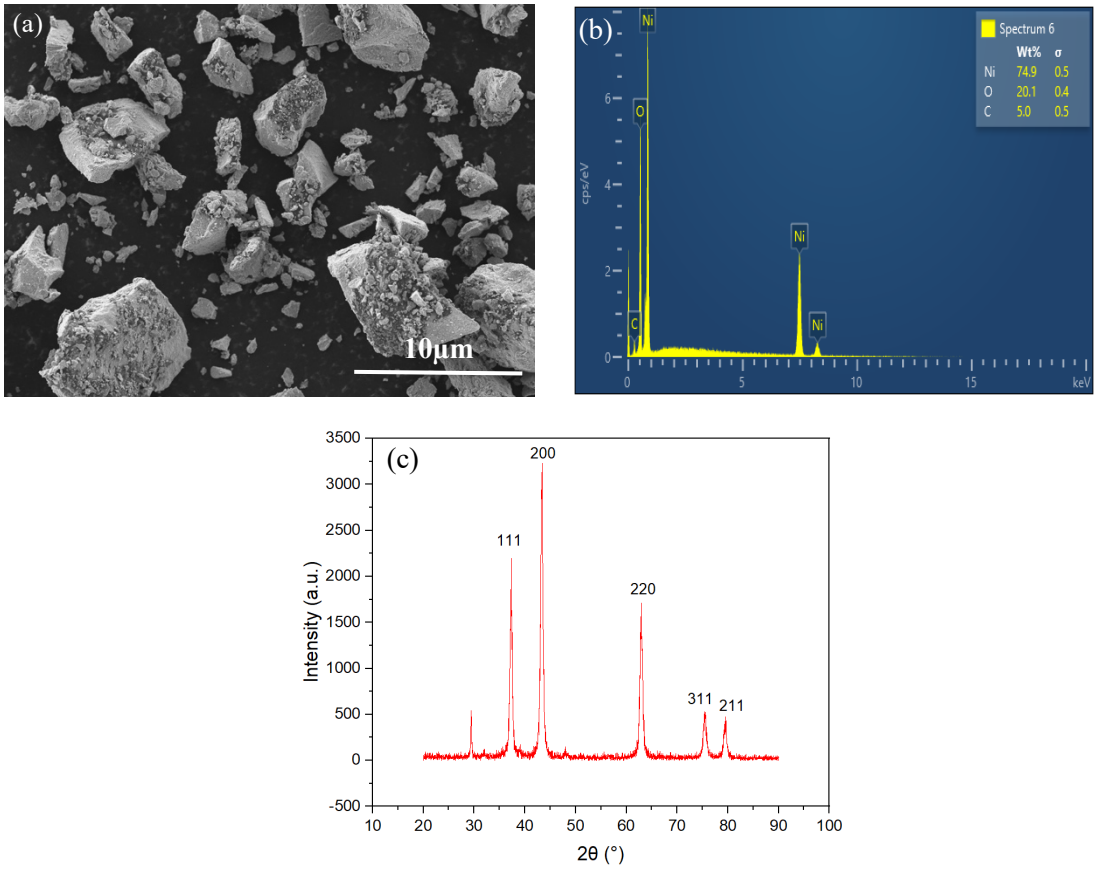

Figure 1: (a) SEM micrograph of NiO calcined at 400 °C (b) EDX spectrum and (c) XRD pattern of NiO

The SEM images in Figure 2 depict the morphology of NC50 and NC513 at 1000x magnification. Figure 2 (a) shows that NC50 consists of slightly larger and more aggregated particles, whereas Figure 2 (b) reveals that NC513 has a more fragmented structure with finer particle distribution. The increased roughness and dispersion observed in NC513, which could enhance electrolyte accessibility within the electrode system.

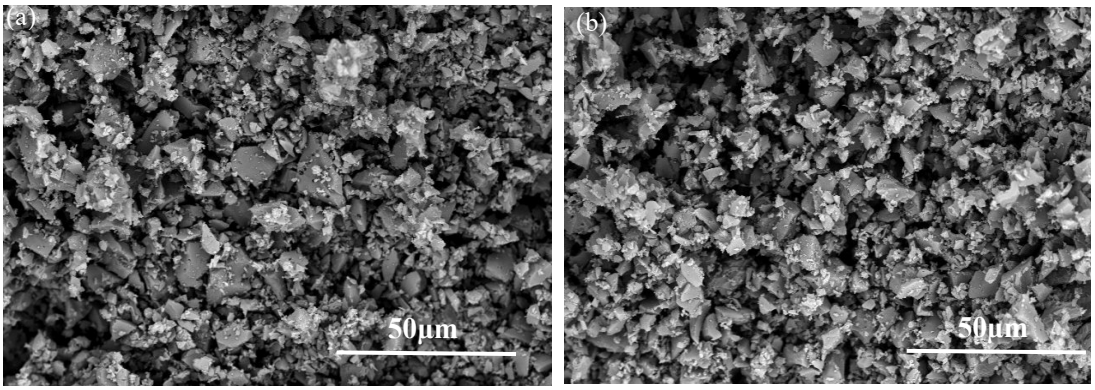

Figure 2: SEM micrographs of (a) NC50 and (b) NC513

3.2 Electrochemical Performance

The electrochemical performance of four electrodes (NC50, NC513, NC511, and NC531) was evaluated to determine their capacitive behavior. LSV was used to investigate the maximum potential limit of the 15 M $Ca(NO_3)_2$ electrolyte, as shown in Figure 3. The LSV curves indicate that the 15 M $Ca(NO_3)_2$ electrolyte exhibits electrochemical stability up to 2.5 V at a scan rate of 0.1 V s^{-1}, both with and without NiO in the AC-based electrodes. Notably, this result demonstrates that incorporating NiO into the electrode does not compromise the electrolyte's stability. The observed stability of 2.5 V for the $Ca(NO_3)_2$ electrolyte is comparable to the ESW reported for other nitrate-based WiSE systems in previous studies. For example, an 11 M $NaNO_3$ electrolyte exhibited an ESW of 2.3 V [15], while a 12M $NaNO_3$ electrolyte demonstrated stability up to 2.56 V [16]. Additionally, a $LiNO_3$-based electrolyte showed an ESW of 2.2 V [17]. This highlights the competitive stability of $Ca(NO_3)_2$ as an alternative nitrate-based electrolyte.

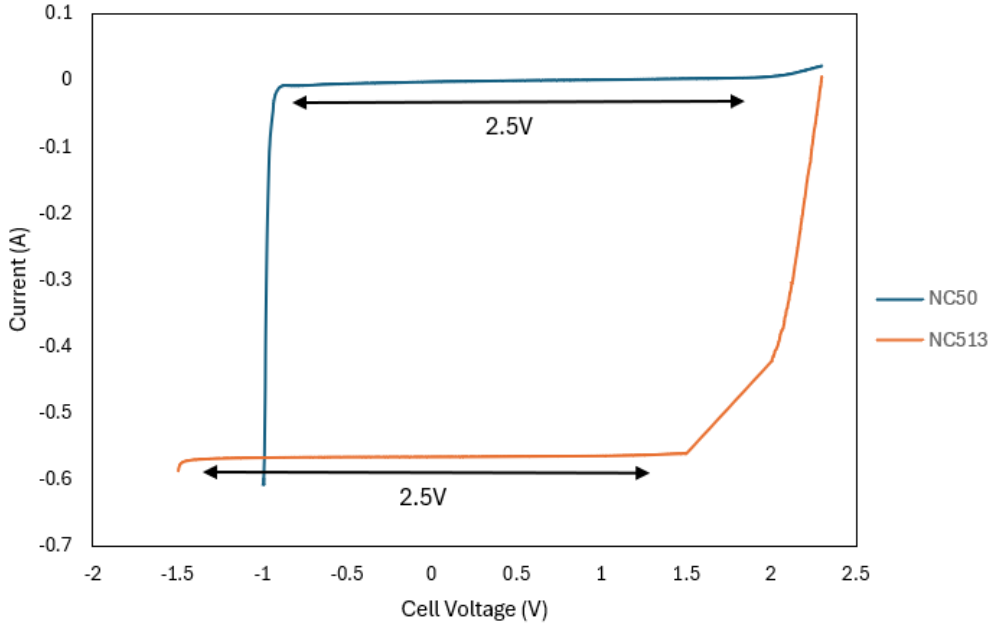

Figure 3: LSV for NC50 and NC513 in 15M $Ca(NO_3)_2$ electrolyte with frequencies ranging from 0.01 to 100 000 Hz

3.2.1 Cyclic Voltammetry (CV)

Figure 4 (a) presents the CV profiles of NC50, NC513, NC511, and NC531 electrodes at scan rate of 10 m Vs^{-1} in 15 M $Ca(NO_3)_2$ electrolyte. The specific capacitance, calculated using Equation (1) and illustrated in Figure 4 (b), reveals that NC513 achieves the highest specific capacitance of 35.32 F g^{-1}, surpassing pure AC electrode (NC50) at 33.45 F g^{-1}. However, further increasing NiO content in NC511 and NC531 results in a decline in specific capacitance to 28.80 F g^{-1} and 18.02 F g^{-1}, respectively. NiO has a BET surface area of 40.58 m^2 g^{-1}, and its excessive presence in NC511 and NC531 reduces the overall surface area of the NiO/AC electrode, thereby limiting conductivity and ion accessibility [11,18]. NiO is inherently hydrophilic, forming Ni-OH (nickel hydroxide) species on its surface when exposed to air or moisture. This hydroxyl (-OH) groups enhance surface wettability [19], thus improving WiSE electrolyte penetration. However, when NiO content exceeds 50% (NC531), electrochemical performance declines further compared to NC50 due to the reduced surface area of the NiO/AC electrode. Excessive NiO reduces active surface area and ion diffusion pathways, increasing resistance and limiting charge storage capacity. Optimizing NiO content is essential to achieving a balance between ionic conductivity and surface area for enhanced supercapacitor performance.

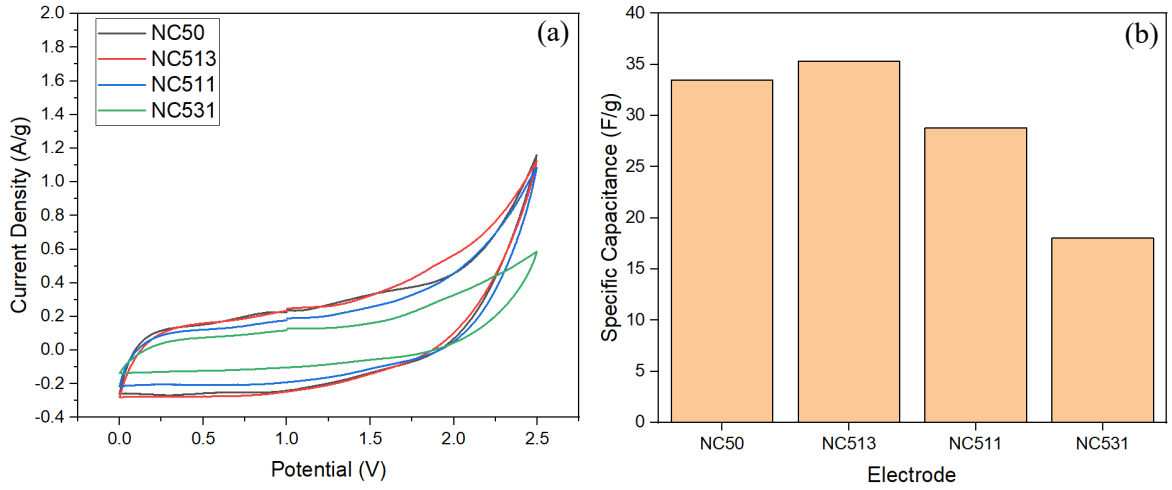

Figure 4: (a) CV curves at a scan rate of 10 m Vs^{-1} s and (b) specific capacitance at scan rates of 10 m Vs^{-1} for NC50, NC513, NC511, and NC531

3.2.2 Galvanostatic charge-discharge (GCD)

The electrodes were further evaluated using GCD analysis at a constant current density of 0.5 A g^{-1} to assess charge storage performance. The GCD curves in Figure 5 (a) exhibit nearly triangular shapes for all electrodes, confirming EDLC behavior. Figure 5 (b) shows that NC50 has the highest iR drop of 0.39 V, indicating greater internal resistance. In contrast, NC513 achieves the lowest at 0.1 V, representing a 75% reduction of iR drop as compared to N50, signifying improved conductivity and ion transport. As NiO content increased in NC511 and NC531, higher iR drop of 0.14 V and 0.17 V respectively, were observed in Figure 5(b), due to its low electrical conductivity, hindering charge transfer and increasing Ohmic resistance [20]. Nevertheless, the iR drop in these samples remains lower than in NC50. This trend aligns with SEM results (Figure 2), where NC513 shows finer, well-dispersed particles which promote better electrolyte penetration and charge transfer. Whereas NC50 shows larger, and agglomerates particles contribute to higher resistance.

Energy and power densities were calculated using Equations (2) and (3). NC513 achieves the highest energy density of 9.96 $Whkg^{-1}$ at 500 Wkg^{-1}, surpassing NC50 (7.69 $Whkg^{-1}$), thereby highlighting NiO's contribution to charge storage. However, because NiO has a lower surface area (40.58 m^2 g^{-1}) than AC, its excessive presence in NC511 and NC531 reduces the overall surface area of the NiO/AC electrode, which limits conductivity and ion accessibility. These findings confirm that NiO content above 50% decreases performance, aligning with Yadav and Tripathi [10], who investigated 1:1, 1:2, and 1:3 in weight ratio of AC/NiO in 6 M KOH. The study reported that a 1:1 NiO/AC ratio (50% of NiO) exhibited the best performance, achieving an energy density of 5.0 Wh kg^{-1} at 300 W kg^{-1}.

In this work, NC513, with only 25% NiO, demonstrates significantly a 99.2% higher energy density compared to Yadav and Tripathi [10]. This could be likely due to the wider electrochemical stability window of $Ca(NO_3)_2$ and NiO's role in enhancing ion transport.

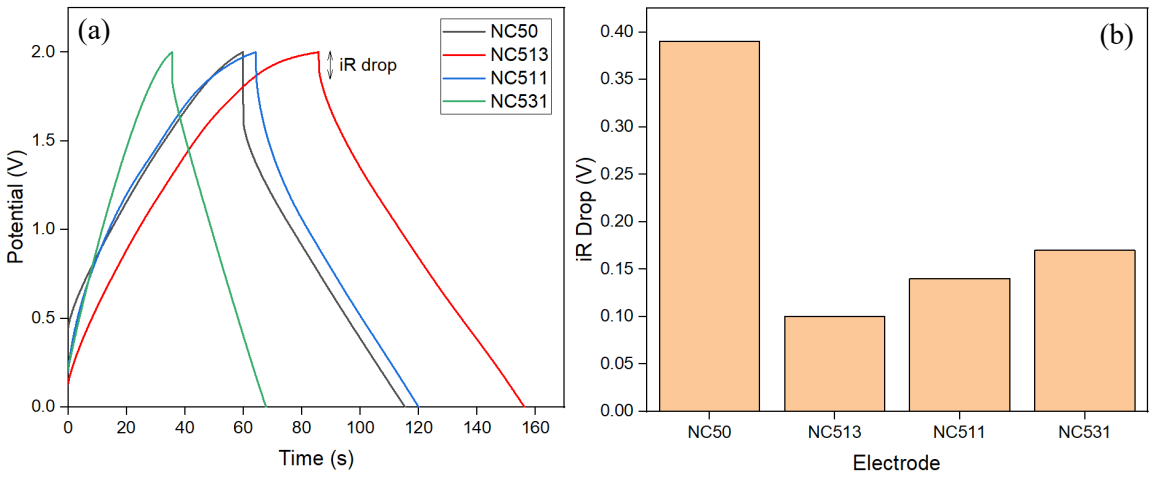

Figure 5: (a) GCD curves of NC50, NC513, NC511 and NC531 electrodes at 0.5 A g^{-1} and (b) iR drop values for all formulated electrodes based on GCD analysis

3.2.3 Electrochemical Impedance Spectroscopy (EIS)

EIS measurements were conducted with frequencies ranging from 0.01 to 100 000 Hz. Figure 6 illustrates that all electrodes display semicircles in the high-frequency region and Warburg lines in the low-frequency region. NC50 shows the largest semicircle in the high-frequency region, indicative of higher charge transfer resistance (Rct) at the electrode/electrolyte interface [3]. In contrast, NC513 exhibits the smallest semicircle, reflecting lower Rct and improved electrochemical performance. This aligns with the lower iR drop observed in GCD analysis. NC511 and NC531 exhibit intermediate semicircles, consistent with GCD results. The steeper Warburg slope of NC513 suggests enhanced ion diffusion, further supported by its SEM analysis in Figure 2 (b), where finer particle distribution improves electrolyte penetration and electrode-electrolyte interaction.

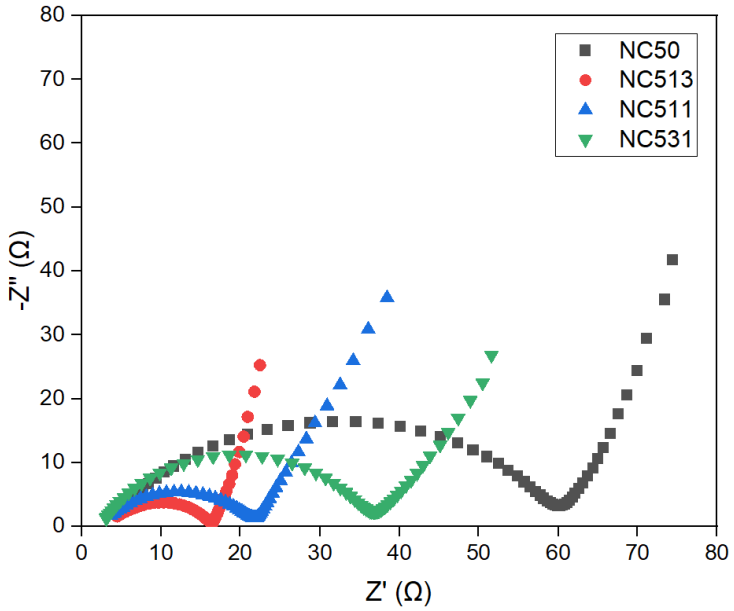

Figure 6: Nyquist plots of NC50, NC513, NC511 and NC531 electrodes in 15 M $Ca(NO_3)_2$ electrolyte

4. CONCLUSIONS

Incorporating NiO not more than 50% into AC electrodes as composite electrode could enhance supercapacitor performance in $Ca(NO_3)_2$ by improving charge transfer efficiency and reducing internal resistance. NC513 achieves the highest energy density of 9.96 Wh kg^{-1} at 500 W kg^{-1}, a 29.5% increase over NC50 (7.69 Wh kg^{-1}). The iR drop trend in GCD follows NC513 < NC511 < NC531 < NC50, with NC513 exhibiting the lowest iR drop (0.1 V) and the smallest semicircle in EIS analysis as compared to NC50, indicating reduced resistance. SEM analysis further supports these findings, revealing a fragmented structure and increased roughness in NC513, which enhances electrolyte accessibility. Thus, optimizing NiO content in NiO/AC electrode is crucial for developing high-performance supercapacitors with improved efficiency and stability.

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Author Contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of Conflict of Interest

The authors have no disclosures to declare.

Compliance with Ethical Standards

The work is compliant with ethical standards.

References

[1] Energy Storage Systems Market Size, Share, and Trends 2024 to 2034 (2024). [Online]. [Accessed 22nd November 2024]. Available from World Wide Web: https://www.precedenceresearch.com.

[2] Yadlapalli, R. T., Alla, R. R., Kandipati, R., & Kotapati, A. (2022). Super capacitors for energy storage: Progress, applications and challenges. *Journal of Energy Storage*. 49, 104194.

[3] Farm, Y. Y. (2020). Biomass derived activated carbon as electrode materials for electrochemical double layer capacitors (EDLC). (Doctoral dissertation, University of Sheffield). pp. 9–115.

[4] Scarcello, A., Alessandro, F., Cruz Salazar, Y., Arias Polanco, M., Vacacela Gomez, C., Tene, T., Guevara, M., Bellucci, S., Straface, S., & Caputi, L. S. (2023). Stable supercapacitors based on activated carbon prepared from italian orange juice. *Nanomaterials*. 14(1),71.

[5] Jayakumar, S., Santhosh, P. C., Mohideen, M. M., & Radhamani, A. V. (2023). A comprehensive review of metal oxides (RuO_2, Co_3O_4, MnO_2 and NiO) for supercapacitor applications and global market trends. *Journal of Alloys and Compounds*. 976, 173170.

[6] Liang, R., Du, Y., Xiao, P., Cheng, J., Yuan, S., Chen, Y., Yuan, J. & Chen, J. (2021). Transition metal oxide electrode materials for supercapacitors: a review of recent developments. *Nanomaterials*. 11(5), 1248.

[7] Liu, J., Bao, J., Zhang, X., Gao, Y., Zhang, Y., Liu, L., & Cao, Z. (2022). MnO_2-based materials for supercapacitor electrodes: challenges, strategies and prospects. *RSC Advances.* 12(55), 35556-35578.

[8] Bulla, M., Kumar, V., Devi, R., Kumar, S., Sisodiya, A. K., Dahiya, R. & Mishra, A. K. (2024). Natural resource-derived NiO nanoparticles via aloe vera for high-performance symmetric supercapacitor. *Scientific Reports*. 14(1), 7389.

[9] Cao, Y., He, Y., Gang, H., Wu, B., Yan, L., Wei, D. & Wang, H. (2023). Stability study of transition metal oxide electrode materials. *Journal of Power Sources*. 560, 232710.

[10] Yadav, M. S. & Tripathi, S. K. (2017). Synthesis and characterization of nanocomposite NiO/activated charcoal electrodes for supercapacitor application. *Ionics*. 23(10), 2919-2930.

[11] Lota, K., Sierczynska, A. & Lota, G. (2011). Supercapacitors based on nickel oxide/carbon materials composites. *International Journal of Electrochemistry*. 2011(1), 321473.

[12] Gong, K., Lee, H., Choi, Y., Jung, G., Keum, K., Kim, J. W. & Ha, J. S. (2024). A flexible supercapacitor with high energy density and wide range of temperature tolerance using a high-concentration aqueous gel electrolyte. *Electrochimica Act.* 475, 143585.

[13] Yumak, T., Bragg, D. & Sabolsky, E. M. (2019). Effect of synthesis methods on the surface and electrochemical characteristics of metal oxide/activated carbon composites for supercapacitor applications. *Applied Surface Science*. 469, 983-993.

[14] El Halimi, M. S., Zanelli, A., Soavi, F. & Chafik, T. (2023). Building towards supercapacitors with safer electrolytes and carbon electrodes from natural resources. *World*. 4(3), 431-449.

[15] Thareja, S. & Kumar, A. (2021). “Water-in-salt” electrolyte-based high-voltage (2.7 V) sustainable symmetric supercapacitor with superb electrochemical performancen - an analysis of the role of electrolytic ions in extending the cell voltage. *ACS Sustainable Chemistry & Engineering*. 9(5), 2338-2347.

[16] Guo, J., Ma, Y., Zhao, K., Wang, Y., Yang, B., Cui, J. & Yan, X. (2019). High-performance and ultra-stable aqueous supercapacitors based on a green and low-cost water-in-salt electrolyte. *ChemElectroChem*. 6(21), 5433-5438.

[17] Tulaphon, P., Tantitumrongwut, P., Ditkanaruxkul, T., Bunpheng, A., Tangthana-umrung, K., Chomkhuntod, P. & Iamprasertkun, P. (2023). High voltage aqueous based energy storage with “Water-in-LiNO3” electrolyte. *Chemical Engineering Journal Advances*. 16, 100553.

[18] Qi, Z., Huang, S., Younis, A., Chu, D. & Li, S. (2016). Nanostructured metal oxides-based electrode in supercapacitor applications. *IntechOpen*. 67-88.

[19] Paliwal, M. K. & Meher, S. K. (2019). Hierarchically organized ultrathin NiO nanofibers/highly defective-rGO heteronanocomposite: an advanced electrode material for asymmetric supercapacitors. *Advanced Materials Interfaces*, 6(20), 1900889.

[20] Siddiqui, S. E., Rahman, M. A., Kim, J. H., Sharif, S. B. & Paul, S. (2022). A review on recent advancements of Ni-NiO nanocomposite as an anode for high-performance lithium-ion battery. *Nanomaterials*. 12(17), 2930.