

Article

Cu-Cu₂O/ZrO₂ Mixed Oxide by Self-Sustained Combustion of Amorphous Ribbons as Electrode Material for Supercapacitor

Mircea Nicolaescu ¹, Carmen Lazau ¹, Corina Orha ¹, Cosmin Codrean ² and Cornelia Bandas ^{1,*}

¹ Condensed Matter Department, National Institute for Research and Development in Electrochemistry and Condensed Matter, A. P. Podeanu Street, No 144, 300569 Timisoara, Romania; mircea.nicolaescu@incmc.ro (M.N.); carmen.lazau@incmc.ro (C.L.); corina.orha@incmc.ro (C.O.)

² Department of Materials and Manufacturing Engineering, Faculty of Mechanical Engineering, Politehnica University Timisoara, P-ta Victoriei, No. 2, 300006 Timisoara, Romania; cosmin.codrean@upt.ro

* Correspondence: cornelia.bandas@incmc.ro

Abstract

Recently, numerous synthesis methods have been developed for the preparation of nanostructured materials for supercapacitor applications, and top-down strategies have gained increasing attention due to their relative simplicity and reduced processing complexity. In particular, the combustion method is recognized as one of the simplest and most rapid approaches for producing a wide range of materials. Within this study, the combustion of Cu₄₈Zr₄₇Al₅ amorphous ribbons was employed, and the supercapacitor electrodes based on Cu-Cu₂O/ZrO₂ mixed oxide were developed. The morpho-structural properties of the materials were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM), and the electrochemical performance, particularly for supercapacitor applications, was evaluated by cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) measurements. The CV curves indicate that the Cu–Cu₂O/ZrO₂ mixed oxide structure acts as a positive electrode and exhibits a non-rectangular shape, confirming pseudocapacitive behavior of the as-synthesized material. A maximum areal specific capacitance of 472.7 mF cm^{−2} was obtained at a scan rate of 5 mV s^{−1}. From GCD analysis, an areal specific capacitance of 336.5 mF cm^{−2} was achieved at a current density of 1 mA cm^{−2}. Cycling stability was evaluated over 1000 charge–discharge cycles, showing an increase in capacitance to 135.14% after the 1000th cycle, attributed to the progressive activation of the electrode material. This study highlights the potential of Cu–Cu₂O/ZrO₂ mixed oxides prepared via self-sustained combustion as efficient and durable electrode materials for supercapacitors. The findings provide a starting point for the future optimization of amorphous alloys for the synthesis of mixed-oxide materials through a scalable fabrication process, paving the way for advanced energy storage applications.

Keywords: combustion; mixed oxide; supercapacitors; amorphous ribbons

Academic Editor: Guanjie He

Received: 3 June 2026

Revised: 24 June 2026

Accepted: 29 June 2026

Published: 30 June 2026

Copyright: © 2026 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

1. Introduction

In recent years, to address climate change and global warming, the research community has prioritized the development of renewable and sustainable energy storage technologies, due to the fact that energy consumption is becoming increasingly prevalent in all aspects of life. Among non-conventional devices, supercapacitors, batteries and fuel cells are most widely used in electric vehicles and electronic devices,

in which through electrochemical reactions the chemical energy is converted into electrical energy [1]. The increasing demand for supercapacitors (SCs), also known as electrochemical capacitors, is highlighted by their fast charge–discharge rate, greater stability, high specific power, high capacitance, and a long cycle life. Another important role for fabrication of SCs is played by the electrode material, that should possess large specific surface area, environmental compatibility, and high conductivity. The performance of SCs is primarily influenced by the kinetic characteristics and active surface area of the electrode materials; therefore, the choosing of the electrode materials with high electrical properties and good pore structure is very important [2]. Among material classes seen as adequate potential candidates for supercapacitor applications, transition metal oxides (TMO) [3–5], carbons [6,7], and MOFs [8] are well studied as electrode materials, with the pseudocapacitive nature of these materials being linked to rapid and reversible reactions at the material surface.

Different metal oxides have been used as electrode material for fabrication of supercapacitors, such as NiO, ZnO, Fe₂O₃, TiO₂, MnO₂, RuO₂, and Cu₂O [1,9]. While these materials are promising in terms of energy density, there are some limitations for industrial usage because of their low conductivity, unstable volumetric transformation, and poor ion diffusion in the bulk phase [10]. Among them, CuO nanostructures have recently attracted high interest in the research community due to their low cost, non-toxicity and easy synthesis of various nanostructures [11–13]. Generally, copper oxide has been investigated as single (CuO or Cu₂O) or double (CuO–Cu₂O) compounds highly significant in environmental application, energies, catalysis, batteries and supercapacitors [14]. The excellent physico-chemical properties together with the low cost and simple synthesis methods, make CuO–Cu₂O structures a great candidate for supercapacitors. Kumar et al. obtained CuO–Cu₂O nanoscrubbers by a simple chemical method and evaluated the electrode for high-performance pseudo-supercapacitors applications, being highly stable for 2000 cycles at 2 A g^{−1} [14]. Zhou et al. reported design and fabrication of the CuO/Cu₂O@NiCo₂S₄ core–shell nanostructures for electrode materials, exhibiting ultrahigh specific capacitance and a high-rate performance for supercapacitor application [2]. Lately, many researchers have investigated positive effects from incorporating ZrO₂ in copper as a support or promotor. ZrO₂, a metal oxide with excellent properties, such as high thermal stability, high corrosion resistance, and low light absorption, exhibits three crystalline phases under atmospheric pressure: monoclinic—the most stable [15], cubic and tetragonal [16,17]. In our previous work, Nicolaescu et al. reported a thermal oxidation of Cu₄₈Zr₄₇Al₅ amorphous ribbons to form Cu–Zr mixed metal oxides for electrochemical application [18]. Thermal oxidation of amorphous ribbons is an interesting method for producing hetero-structure metal oxide, and can be successfully extended to other metallic alloys for synthesizing nanostructured metal oxides. Over time, different techniques such as sol–gel, hydrothermal, co-precipitation or impregnation, and combustion were applied to transform a metal oxide into another oxide. Among them, combustion synthesis is an efficient and homogenous method for the preparation of various metal oxides [19], which requires simple equipment and low-cost reagents, and reduces consumption of energy and time. Self-generating and exothermic reactions between metal salts and organic substances are typically involved in the combustion process [20]. Based on its advantages, the combustion method satisfies the demands of the green and sustainable modern industry, and recently some researchers have proposed a novel approach to expand this technique to the combustion of metal elements (rather than metal salts) in their solid amorphous phase, which results in nanostructured oxides [21]. The use of amorphous alloys in combustion synthesis highlights their ability to exploit metastability and compositional uniformity, enabling the formation of uniformly dispersed mixed oxides through self-propagating reactions. Li et al. reported the

combustion of CuZr amorphous ribbons to obtain ZrO₂-containing copper oxides with enhanced catalytic properties, which can be theoretical applied to many other material systems to synthesize multifunctional nanomaterial [21]. Renuka et al. synthesized ZrO₂/CuO nanocomposites by a facile combustion synthesis using oxalyl dihydrazide (ODH) as fuel [19].

In this study, we report the combustion synthesis of Cu₄₈Zr₄₇Al₅ amorphous ribbons to obtain Cu–Cu₂O/ZrO₂ mixed oxides, which are explored for the first time as functional materials in energy storage applications as supercapacitor electrodes.

2. Materials and Methods

2.1. Fabrication of the Supercapacitor's Electrodes

The melt-spinning method was used to produce amorphous Cu₄₈Zr₄₇Al₅ ribbons with continuous geometry and uniform dimensions, having a thickness of 25 µm and a width of 1.5 mm. The detailed experimental procedure has been described in our previous work [18]. The combustion of the Cu₄₈Zr₄₇Al₅ ribbons was carried out in an air atmosphere, and the self-sustained combustion process is presented in the Supplementary Materials as Video S1. After combustion, the resulting products were ground in an agate mortar to obtain a rather homogeneous material. Supercapacitor electrode materials were achieved by blending the Cu–Cu₂O/ZrO₂ mixed oxide (80 wt%) with carbon black (10 wt%) and polyvinylidene fluoride (PVDF, 10 wt%) in N-methylpyrrolidone to obtain a uniform slurry. The resulting mixture was then coated on to a stainless steel (SS) substrate with an area of 0.28 cm² and dried at 70 °C.

2.2. Electrode Characterization

The structural characterization was carried out using X-ray diffraction (XRD) analysis with a PANalytical X'Pert PRO MPD diffractometer. Morphological investigations were performed using a Quanta FEG 250 FEI scanning electron microscope (SEM) equipped with an energy-dispersive X-ray (EDX) detector. Electrochemical measurements were conducted in a 1 M KOH supporting electrolyte using a conventional three-electrode cell configuration, consisting of an Ag/AgCl reference electrode, a Cu–Cu₂O/ZrO₂ mixed oxide working electrode, and a platinum wire counter electrode. All electrochemical tests were performed using a PGSTAT 302 potentiostat/galvanostat (Metrohm Autolab B.V.). Cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS) analyses were employed for the electrochemical investigations.

3. Results and Discussion

Figure 1 shows the SEM morphological analysis of the as-synthesized Cu–Cu₂O/ZrO₂ mixed oxide, obtained by the combustion method. Two different areas of the sample were studied, at different magnifications, to highlight the surface morphological features. In the first analyzed area (Figure 1a), a granular and rough structure can be observed, consisting of oxide particles arranged in randomly distributed agglomerates with various morphologies, including spherical and irregular shapes, as well as non-uniform particle sizes. During the combustion process, intense exothermic reactions occur, leading to the formation of rough structures composed of non-uniformly aggregated oxide particles. Furthermore, the differences between the properties of the resulting oxides, such as nucleation rate, or particle growth rates, may contribute to the development of distinct morphologies. In the second analyzed area (Figure 1b), another aspect of the course of the reactions during combustion was highlighted. From the images it can be seen that the material has a porous appearance, and island-like formations have formed, made up of oxide particles with irregular shapes. At the edges of these agglomerations, an uneven

granular texture can be observed, consisting of irregular particles. The formation of voids can be attributed to the evaporation of aluminum during the combustion reaction. The local temperature reached during combustion likely exceeded the evaporation temperature of aluminum, favoring its removal from the structure, as supported by XRD analysis. Figure S1 from Supplementary Materials presents the EDX spectrum, which confirms that Al has been completely removed from the matrix and is not present as a residual amorphous phase.

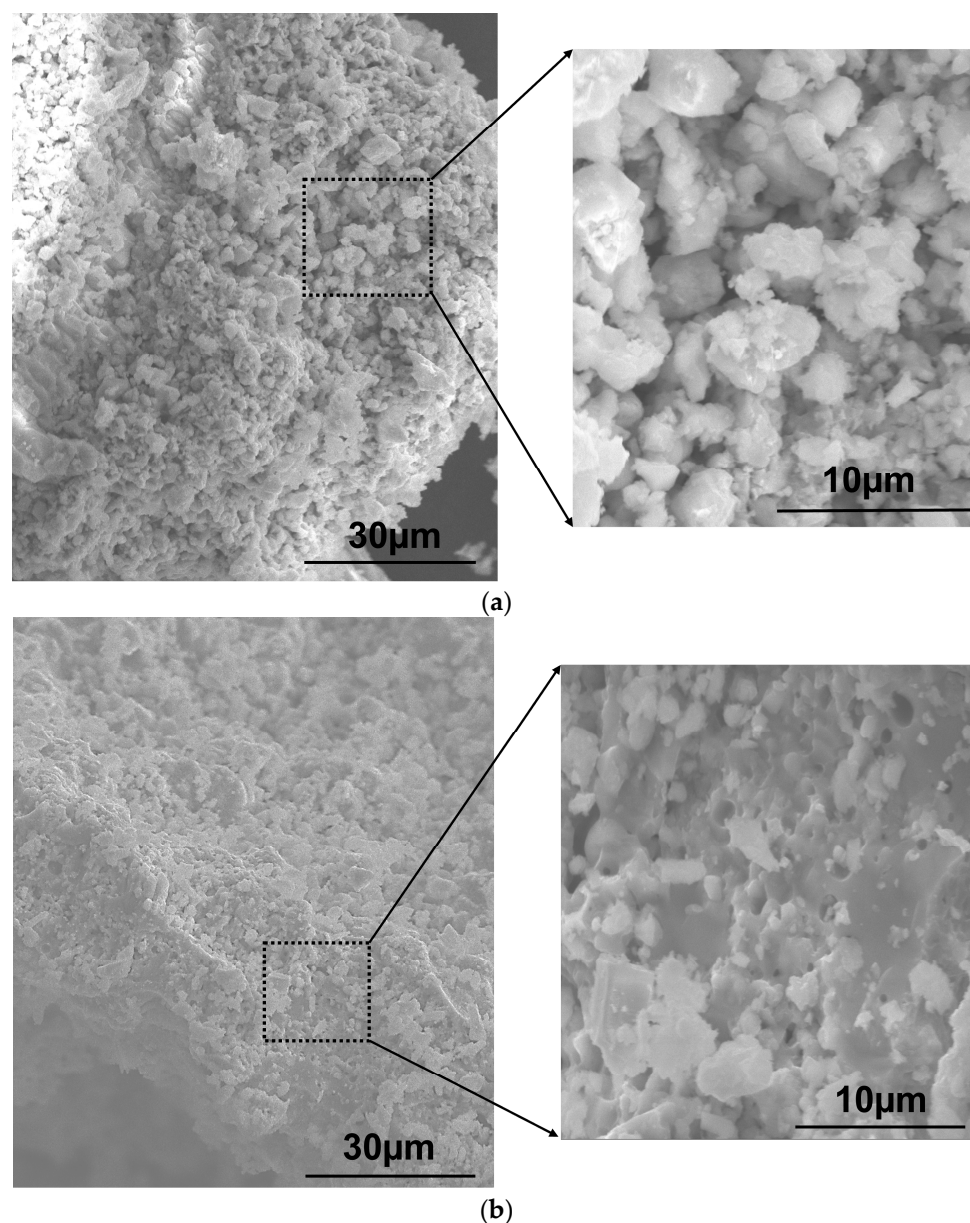


Figure 1. SEM morphology of the as-synthesized material: (a) analyzed area zone 1; (b) analyzed area zone 2.

The structural properties of the oxide materials obtained by the combustion method were investigated by XRD analysis and presented in Figure 2. The diffraction data exhibits sharp diffraction peaks, indicating the crystallization of the samples during the combustion process. Furthermore, the diffraction results reveal the presence of metallic Cu with a cubic crystal structure, corresponding to the (111), (020), and (022) crystallographic planes. During the combustion process, the mixed-oxide material was identified as consisting of polymorphic phases of ZrO_2 together with a cuprous oxide (Cu_2O) phase. ZrO_2 is present in both the monoclinic phase (m- ZrO_2 , JCPDS card No. 00-036-0420) and the tetragonal phase (t- ZrO_2 ,

JCPDS card No. 00-017-0923). These results are consistent with previous studies employing thermal oxidation as the synthesis method [18]. The cubic structure of Cu_2O was identified according to JCPDS card No. 96-900-7498, indicating the subsequent oxidation of metallic Cu during the self-sustained combustion process. No diffraction peaks corresponding to the aluminum phase were detected, suggesting that the combustion temperature exceeded the evaporation temperature of aluminum. This assumption is further supported by the formation of holes observed in the SEM analysis. X. Li and co-workers reported that $\text{Cu}_{60}\text{Zr}_{40}$ amorphous alloys processed by the combustion method predominantly formed copper- and copper oxide-based materials together with monoclinic ZrO_2 . In contrast, the present study demonstrates that increasing the Zr content in the precursor alloy promotes the formation and dominance of zirconium oxide phases in the final combustion products [21].

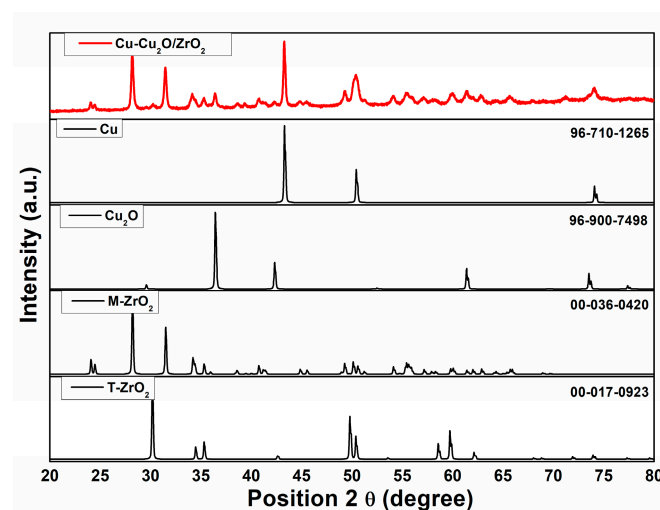


Figure 2. X-ray patterns of the as-synthesized material.

The electrochemical behavior of the $\text{Cu-Cu}_2\text{O/ZrO}_2$ electrode was investigated using the CV technique at different scan rates in 1M KOH supporting electrolyte, as shown in Figure 3a. A potential window of 0 to 0.6 V was selected in accordance with other studies. The electrode exhibited non-rectangular CV curves, indicating that the charge storage mechanism is governed by pseudocapacitive behavior in the electrode material [22].

The CV curves exhibit broad anodic and cathodic features rather than well-defined peaks, suggesting a predominantly capacitive behavior with possible contributions from surface redox processes involving the copper species ($\text{Cu}^0/\text{Cu}^+/\text{Cu}^{2+}$). However, the absence of clearly resolved redox peaks suggests it is likely that electrochemical processes occur over a wide potential range. Such dispersion can be attributed to limited contact between the electrolyte and the electrochemically active surface which results in incomplete conversion of the copper oxide species [23].

A similar argument is difficult to apply to the oxidation state of Zr^{4+} in zirconium, as no distinct redox peaks associated with the zirconium species are clearly visible [24]. We believe that ZrO_2 plays an important synergistic role with the copper species by improving structural stability and preventing agglomeration, thereby leading to enhanced overall electrochemical performance. As reported in the literature, ZrO_2 -based composites exhibit enhanced capacitance retention and electrochemical durability [25,26].

Figure 3b presents the variation in areal specific capacitance (C_{SP}) as a function of scan rate calculated according to Equation (1) [27].

$$C_{\text{SP}} = \frac{A}{k\Delta V} \quad (1)$$

where A—area under the curve; k—scan rate; S—area of the active material (cm^2); and ΔV —potential window.

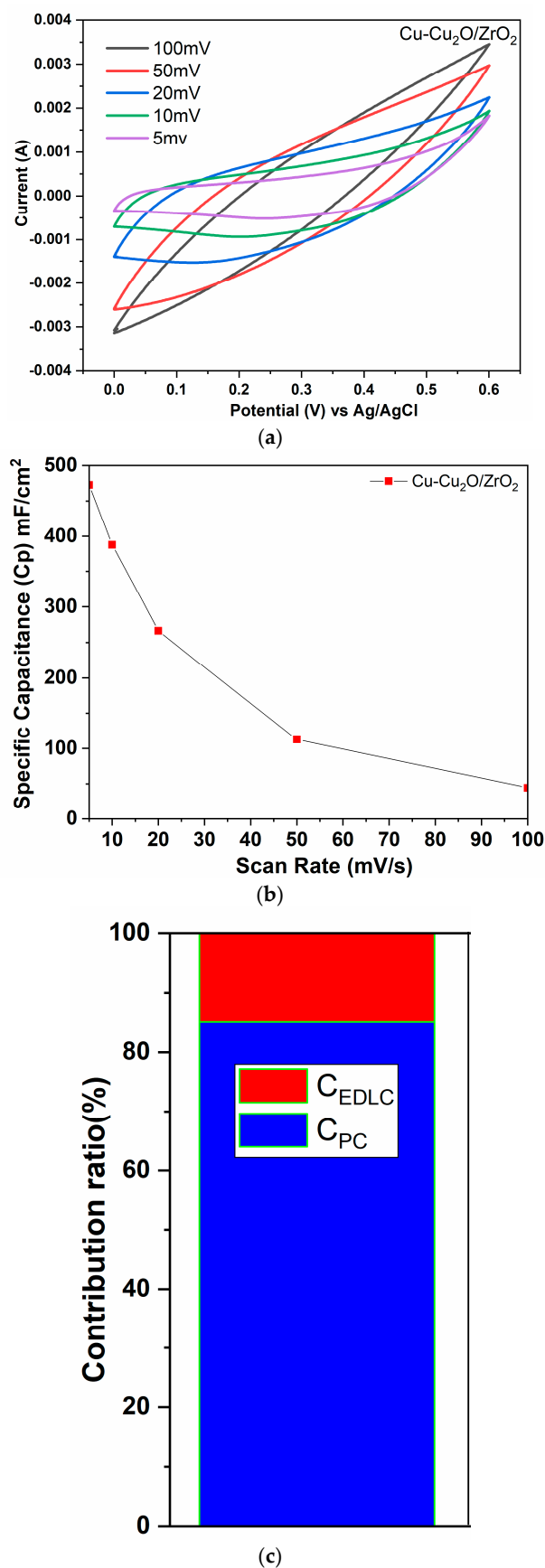


Figure 3. Cyclic voltammograms recorded for Cu–Cu₂O/ZrO₂ electrode (a); plots of specific capacitance vs. potential scan rate of the electrode (b); the contribution ratio (%) of C_{EDLC} vs C_{PC} calculated from Trasatti method (c).

A gradual decrease in specific capacitance with increasing scan rate is observed, which is a typical behavior for supercapacitor electrodes. At low scan rates, electrolyte ions can fully access the active sites of the electrode, resulting in higher capacitance, while at higher scan rates the capacitance decreases due to limited ion diffusion [25,28]. The maximum C_{SP} was 472.7 mF cm^{-2} , obtained at a scan rate of 5 mV s^{-1} , and it decreased linearly to 44.33 mF cm^{-2} at 100 mV s^{-1} , corresponding to a retention rate of 9.37%.

The Trasatti method was used to evaluate the surface-controlled charge component, associated with the electrical double-layer capacitance (CEDLC), and the diffusion-controlled charge component, associated with pseudocapacitance (CPC). The calculations were performed using linear fitting, and the methodology has been described in detail in previous studies [27]. The plots of q versus $v^{-1/2}$ and $1/q$ versus $v^{1/2}$ for the Cu–Cu₂O/ZrO₂ electrode are presented in Figure S2 of the Supplementary Materials. The calculated results indicate that CPC is the dominant contribution, accounting for 85.11% of the total charge storage, while CEDLC contributes 14.89%. These findings demonstrate that the diffusion-controlled charge component is the primary charge-storage mechanism in this material.

The performance of the Cu–Cu₂O/ZrO₂ electrode presented in Figure 4a reveals the charge–discharge (GCD) curves plotted against time at a potential window of 0 to 0.5 V and different current densities 1, 2, 3, 4 and 5 mA cm^{-2} in 1M KOH supporting electrolyte. The GCD curves of the Cu–Cu₂O/ZrO₂ electrode exhibit quasi-linear profiles, indicating the contribution of Faradaic processes associated with pseudocapacitance and involving reversible redox reactions of the copper species, consistent with the CV analysis [23]. IR drop (ΔV_{IR}) values of 0.2 V at 5 mA and 0.067 V at 1 mA show a linear dependence on current, confirming the ohmic nature of the voltage drop and indicating efficient electrode–electrolyte contact [29]. The internal resistance (R_{ESR}) of the electrode was estimated from the IR drop using Equation (2) [30].

$$R = \frac{\Delta V_{IR}}{I} \quad (2)$$

where R —internal resistance; ΔV_{IR} —voltage drop; and I —the applied current.

The calculated resistance remains nearly constant at approximately 40Ω for current values between 2 and 5 mA, and presented a slight increase at 67Ω for 1 mA current density. The slightly higher resistance observed at 1 mA can be attributed to polarization effects at the electrode–electrolyte interface at low current densities [31]. Figure 4b presents the variation in areal specific capacitance (C_{SP}) as a function of current density calculated according to Equation (3) [27].

$$C_{SP} = \frac{I \Delta t}{\Delta V S} \quad (3)$$

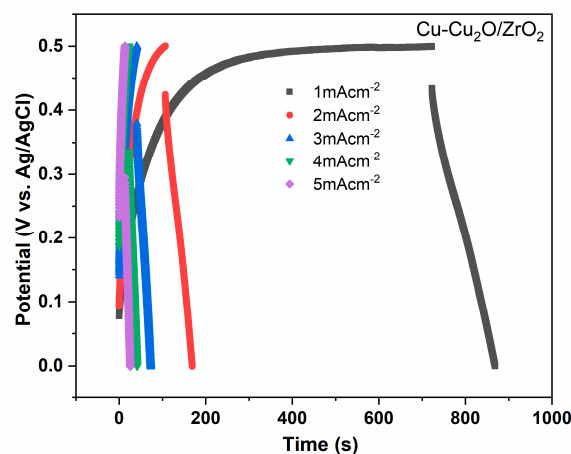
where I —applied current (mA); Δt —discharge time (s); ΔV —discharge voltage (V); and S —area of the active material (cm^2).

A decline in the C_{SP} at higher current densities is also observed. This can be attributed to the limited utilization of the active material, as electrolyte ions do not have sufficient time to fully penetrate the interior of the electrode [27,32]. The maximum C_{SP} was 336.5 mF cm^{-2} , obtained at a current density of 1 mA cm^{-2} , and decreased linearly to $203.54 \text{ mF cm}^{-2}$ at 5 mA cm^{-2} . A high retention rate of 60.47%, compared with the CV analysis, was observed, further confirming the pseudocapacitive behavior of the electrode material. Moreover, the areal Ragone plot of the Cu–Cu₂O/ZrO₂ electrode is presented in Figure 4c, and calculated from the GCD specific energy (E) versus the specific power (P) at different current densities according Equations (4) and (5) [27].

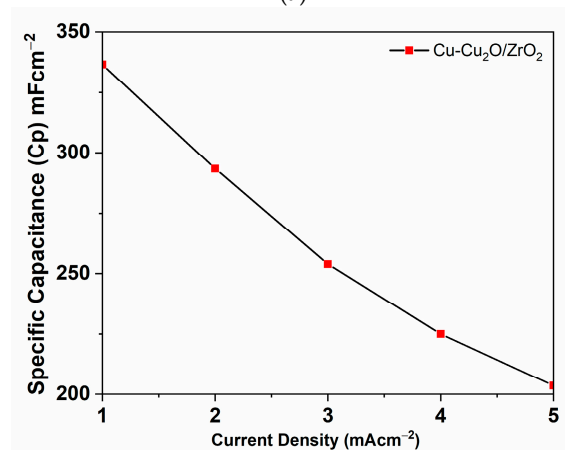
$$E = \left(\frac{C_{SP} \Delta V^2}{2} \right) \quad (4)$$

$$P = \frac{\Delta V I}{2S} \quad (5)$$

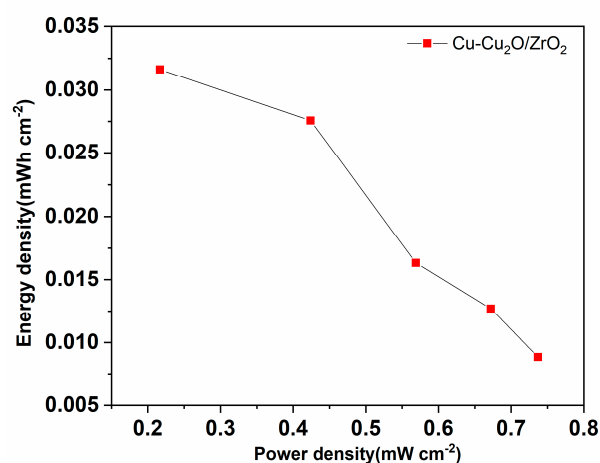
where C_{SP} —specific capacitance; ΔV —discharge voltage; I —applied current; and S —area of the active material.



(a)



(b)



(c)

Figure 4. GCD analysis for Cu–Cu₂O/ZrO₂ electrode (a); specific capacitance vs. current density (b); areal Ragone plot (c).

The electrode delivers a maximum areal energy density of approximately 0.032 m W h cm^{−2} at a low power density of 0.22 m W cm^{−2}. With increasing power density up to 0.73

m W cm⁻², the areal energy density gradually decreases to approximative 0.009 m W h cm⁻², reflecting the typical energy–power trade-off of pseudocapacitive electrodes [33].

Figure 5 presents the Nyquist plots of the Cu–Cu₂O/ZrO₂ electrode in the fresh state (Figure 5a) and after stability testing (Figure 5b) in 1M KOH supporting electrolyte, both including the equivalent circuit inset. Three distinct regions are observed in terms of the frequency. The intercept at high frequencies on the Z' axis represents the ohmic resistance (R_s), which shows a slight decrease from 18 Ω to 15.8 Ω after 1000 cycles, likely due to the decomposition of the insulating surface carbonates of the material during cycling [34]. In the middle-frequency region, the diameter of the semicircle corresponding to the charge transfer resistance (R_{ct}) increases from 5.2 to 20.2 Ω after 1000 cycles. This increase is attributed to diffusion-limited ion transport during cycling [35,36]. In Figure 5a, an interfacial resistance (R_i) is also observed, which disappears upon cycling, indicating that electrolyte wetting and activation of previously inaccessible pores are required to achieve increased capacitance [37]. Furthermore, with cycling (Figure 5b), the semicircle diminishes and an extended Warburg region is formed, enhancing the overall capacitive behavior of the Cu–Cu₂O/ZrO₂ electrode. The activation of additional storage sites leads to higher capacitance at the expense of slower kinetics [24].

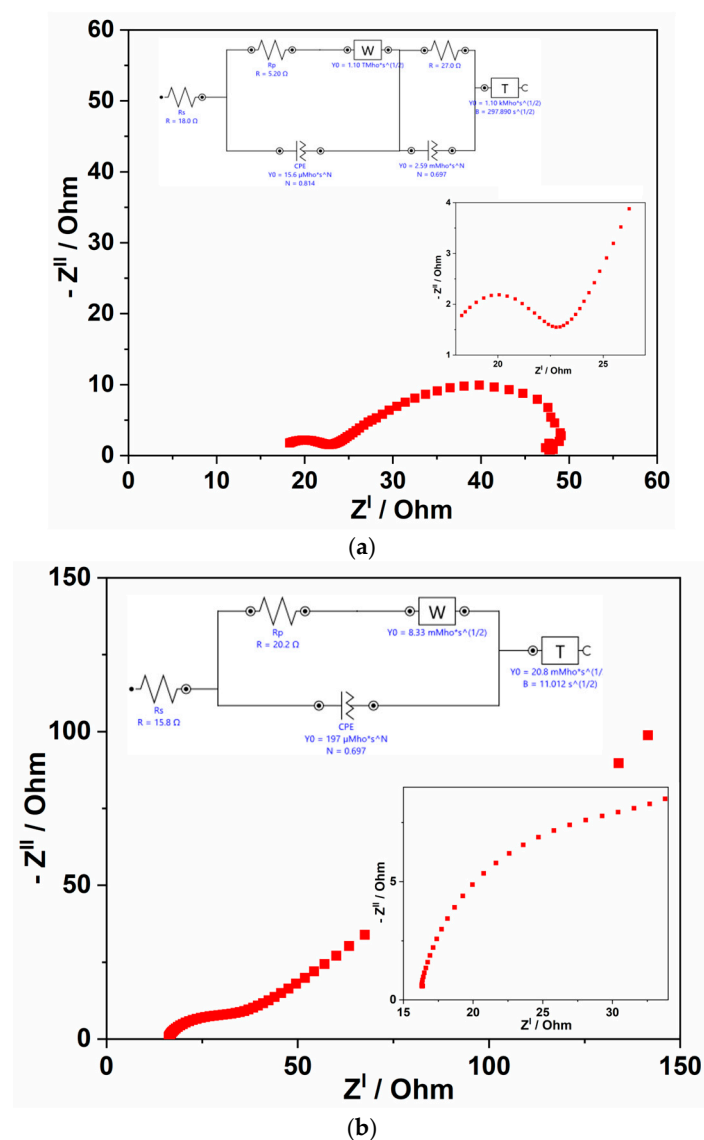


Figure 5. Nyquist plots of Cu–Cu₂O/ZrO₂ electrode: (a) fresh electrode: Insert: equivalent circuit; (b) electrode after 1000 cycles: Insert: equivalent circuit.

The cycling stability of the Cu-Cu₂O/ZrO₂ electrode over 1000 charge–discharge cycles was also evaluated (Figure 6). An initial increase in capacitance is observed during the first half of the cycling process, followed by a gradual decrease, although the capacitance remains higher than the initial value. Overall, after 1000 cycles, the electrode exhibits a positive capacitance retention of 135% [38]. This behavior is consistent with the electrochemical activation process evidenced by the EIS analysis (Figure 5). Furthermore, the increase in discharge time from 16 s to 27 s after 1000 cycles, together with the increase in IR drop, confirms that additional charge storage sites become accessible during cycling [39,40]. The increase in capacitance with cycling is consistent with other research studies. This can be attributed to progressive electrochemical activation. Initially, not all active sites are accessible, but repeated cycling improves ion penetration and activates more redox sites, leading to a higher effective capacitance [41]. During electrochemical activation, more ions penetrate through the channels and reach the electroactive inner Cu₂O/ZrO₂ inside the pockets and activate the inner Cu₂O/ZrO₂ layer of the composite [42]. In Table 1 are presented different structures based on oxide materials for supercapacitor applications in comparison with our work.

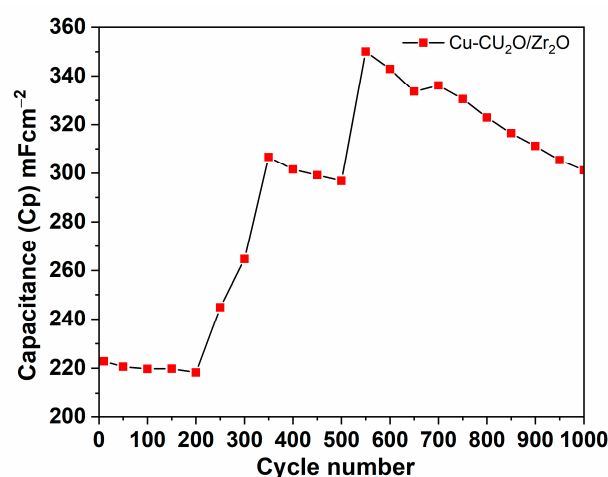


Figure 6. Specific capacitance at 1000 cycles of the as-obtained Cu-Cu₂O/ZrO₂ electrode at a current density of 5 mA cm⁻².

Table 1. Different structures of electrodes used for supercapacitor application.

Electrode Material	Synthesis Method	Electrolyte	Areal/Specific Capacitance	Current Density	Areal/Specific Capacitance	Scan Rate	Cycling Stability	Cycles Number	Energy Density/ Power Density	References
MnO ₂ /CuO/ZrO ₂	Hydrothermal	1 M KOH		-	-119.04 mF/cm ⁻²	5 mV/s ⁻¹	92.10%	5000	0.081 mWhcm ⁻² / 1.3885 mW cm ⁻²	[43]
NPC/Sn ₂ P ₂ O ₇ /CuO	Dealloying	1 M KOH	268.7 mF cm ⁻²	1 mA cm ⁻²	269.36 mF cm ⁻²	5 mV/s ⁻¹	119.68%	500	0.03768 mWhcm ⁻² / 0.2648 mW cm ⁻²	[27]
CuO-Cu ₂ O/copper foam	Anodization method	5 M NaOH	1.23 F cm ⁻²	2 mA cm ⁻²	1.954 F cm ⁻²	2 mV s ⁻¹	120%	5000	-	[44]
Cu ₂ O/Cu	Electrodeposition	1 M KOH	103.6 mF/cm ⁻²	7 mA cm ⁻²	128.6 mF cm ⁻²	5 mV s ⁻¹	83.8%	5000	-	[45]
Cu/Cu ₂ O/CuO (NW)	Thermal oxidation	1 M KOH	21.198 mF cm ⁻²	0.5 mA cm ⁻²	26.158 mF cm ⁻²	5 mV s ⁻¹	110.35%	500	-	[46]
Cu-Cu ₂ O/ZrO ₂	Self-sustained combustion	1 M KOH	336.5 mF cm ⁻²	1 mA cm ⁻²	472.7 mF cm ⁻²	5 mV s ⁻¹	135%	1000	0.032 m W h cm ⁻² / 0.22 m W cm ⁻²	This works

4. Conclusions

The combustion synthesis of the $\text{Cu}_{48}\text{Zr}_{47}\text{Al}_5$ amorphous ribbons successfully produced a crystalline $\text{Cu-Cu}_2\text{O/ZrO}_2$ mixed oxide, also confirmed by the morpho-structural analysis. From XRD we identified the presence of metallic Cu, Cu_2O , and polymorphic ZrO_2 phases, and the absence of aluminum-related peaks suggests its evaporation during the combustion process. This also supports the morphological analysis from SEM together with their surface morphology of as-synthesized materials. The electrochemical analysis demonstrates the pseudocapacitive behavior of the as-synthesized material. The calculated areal specific capacitance, evaluated as a function of scan rate and current density, showed maximum values of 472.7 mF cm^{-2} at a scan rate of 5 mV s^{-1} and 336.5 mF cm^{-2} at a current density of 1 mA cm^{-2} . The EIS analysis of the fresh electrode and after 1000 cycles revealed changes in the resistance mechanisms occurring within the material. These results, in agreement with the cycling stability data, confirm an electrochemical activation process in which the increased capacitance arises from progressive pore wetting and surface activation, while diffusion limited kinetics after long-term cycling.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/batteries12070239/s1>. Figure S1. EDX analysis of as synthesized $\text{Cu-Cu}_2\text{O/ZrO}_2$ sample; Figure S2. Trasatti plot for $\text{Cu-Cu}_2\text{O/ZrO}_2$ electrode; Video S1: Combustion process.

Author Contributions: Conceptualization, M.N., C.C. and C.B.; methodology, M.N., C.L., C.B.; validation, M.N., C.C. and C.B.; investigation, M.N. and C.O.; writing—original draft preparation, M.N., C.L. and C.B.; writing—review and editing, M.N., C.L. and C.B.; visualization, C.L. and C.B.; supervision, C.L. and C.B. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the project “Innovative Technological Approaches to Circularity and Urban-Industrial Symbiosis within the Water-Energy-Materials-Fertilizers Nexus (ECO-NEXUS)”, Smart Growth, Digitalization and Financial Instruments Program, 2021-2027, MySMIS under Grant 336912.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Jayakumar, S.; Santhosh, P.C.; Mohideen, M.M.; Radhamani, A.V. A comprehensive review of metal oxides (RuO_2 , Co_3O_4 , MnO_2 and NiO) for supercapacitor applications and global market trends. *J. Alloys Compd.* **2024**, *976*, 173170. <https://doi.org/10.1016/j.jallcom.2023.173170>.
2. Zhou, L.; He, Y.; Jia, C.; Pavlinek, V.; Saha, P.; Cheng, Q. Construction of Hierarchical $\text{CuO/Cu}_2\text{O@NiCo}_2\text{S}_4$ Nanowire Arrays on Copper Foam for High Performance Supercapacitor Electrodes. *Nanomaterials* **2017**, *7*, 273. <https://doi.org/10.3390/nano7090273>.
3. George, N.S.; Jose, L.; Aravind, A. Review on Transition Metal Oxides and Their Composites for Energy Storage Application. In *Updates on Supercapacitors*; IntechOpen: London, UK, 2022.
4. Li, B.; Dai, F.; Xiao, Q.; Yang, L.; Shen, J.; Zhang, C.; Cai, M. Nitrogen-doped activated carbon for a high energy hybrid supercapacitor. *Energy Environ. Sci.* **2016**, *9*, 102–106. <https://doi.org/10.1039/C5EE03149D>.
5. Gawli, Y.; Banerjee, A.; Dhakras, D.; Deo, M.; Bulani, D.; Wadgaonkar, P.; Shelke, M.; Ogale, S. 3D Polyaniline Architecture by Concurrent Inorganic and Organic Acid Doping for Superior and Robust High Rate Supercapacitor Performance. *Sci. Rep.* **2016**, *6*, 21002. <https://doi.org/10.1038/srep21002>.

6. Soundarya, D.; Sandhiya, M.; Sampathkumar, P.; Suresh, C.; Sathish, M.; Mathiyarasu, J. Doable high energy density supercapacitors using rice husk-derived carbon in dihydroxybenzenes as redox-additive electrolytes. *J. Energy Storage* **2023**, *74*, 109407. <https://doi.org/10.1016/j.est.2023.109407>.
7. Zhu, Y.; Chen, M.; Zhang, Y.; Zhao, W.; Wang, C. A biomass-derived nitrogen-doped porous carbon for high-energy supercapacitor. *Carbon* **2018**, *140*, 404–412. <https://doi.org/10.1016/j.carbon.2018.09.009>.
8. Ghosh, T.K.; Sahu, K.K.; Shanmugam, R.; Rao, H.S.; Gupta, A.; Rao, G.R. Rationally designed FeCoX (X = O, S, Se) nanostructures derived from needle-shaped FeCo-NH₂-BDC MOF for enhanced supercapattery applications. *J. Energy Storage* **2025**, *108*, 115093. <https://doi.org/10.1016/j.est.2024.115093>.
9. Bandas, C.; Orha, C.; Nicolaescu, M.; Morariu, M.-I.; Lăzău, C. 2D and 3D Nanostructured Metal Oxide Composites as Promising Materials for Electrochemical Energy Storage Techniques: Synthesis Methods and Properties. *Int. J. Mol. Sci.* **2024**, *25*, 12521. <https://doi.org/10.3390/ijms252312521>.
10. An, C.; Wang, Y.; Huang, Y.; Xu, Y.; Jiao, L.; Yuan, H. Porous NiCo₂O₄ nanostructures for high performance supercapacitors via a microemulsion technique. *Nano Energy* **2014**, *10*, 125–134. <https://doi.org/10.1016/j.nanoen.2014.09.015>.
11. Xu, P.; Liu, J.; Liu, T.; Ye, K.; Cheng, K.; Yin, J.; Cao, D.; Wang, G.; Li, Q. Preparation of binder-free CuO/Cu₂O/Cu composites: A novel electrode material for supercapacitor applications. *RSC Adv.* **2016**, *6*, 28270–28278. <https://doi.org/10.1039/C6RA00004E>.
12. Zhang, J.; Zhang, G.; Luo, W.; Sun, Y.; Jin, C.; Zheng, W. Graphitic Carbon Coated CuO Hollow Nanospheres with Penetrated Mesochannels for High-Performance Asymmetric Supercapacitors. *ACS Sustain. Chem. Eng.* **2017**, *5*, 105–111. <https://doi.org/10.1021/acssuschemeng.6b00755>.
13. Yang, Y.; Pei, L.; Xu, X.; Xu, J.; Shen, J.; Ye, M. In-situ growth of self-assembled 3D Cu₂O@Cu foam with enhanced electrochemical properties. *Electrochim. Acta* **2016**, *221*, 56–61. <https://doi.org/10.1016/j.electacta.2016.10.150>.
14. Dhilip Kumar, R.; Sreevani, K.; Radhika, G.; Sethuraman, V.; Shanmugavalli, V.; Nagarani, S.; Balachandran, S.; Kumar, M. One-Pot synthesis of CuO-Cu₂O nanoscrubbers for high-performance pseudo-supercapacitors applications. *Mater. Sci. Eng. B* **2022**, *281*, 115755. <https://doi.org/10.1016/j.mseb.2022.115755>.
15. Vaidya, S.; Ahmad, T.; Agarwal, S.; Ganguli, A.K. Nanocrystalline Oxalate/Carbonate Precursors of Ce and Zr and Their Decompositions to CeO₂ and ZrO₂ Nanoparticles. *J. Am. Ceram. Soc.* **2007**, *90*, 863–869. <https://doi.org/10.1111/j.1551-2916.2007.01484.x>.
16. Tran, T.V.; Nguyen, D.T.C.; Kumar, P.S.; Din, A.T.M.; Jalil, A.A.; Vo, D.-V.N. Green synthesis of ZrO₂ nanoparticles and nanocomposites for biomedical and environmental applications: A review. *Environ. Chem. Lett.* **2022**, *20*, 1309–1331. <https://doi.org/10.1007/s10311-021-01367-9>.
17. Hassan, N.S.; Jalil, A.A. A review on self-modification of zirconium dioxide nanocatalysts with enhanced visible-light-driven photodegradation of organic pollutants. *J. Hazard. Mater.* **2022**, *423*, 126996. <https://doi.org/10.1016/j.jhazmat.2021.126996>.
18. Nicolaescu, M.; Orha, C.; Dabici, A.; Hididis, P.; Codrean, C.; Șerban, V.A. Production of Cu-Zr mixed metal oxides by thermal oxidation of amorphous ribbons. *Mater. Today Proc.* **2021**, *45*, 4337–4343. <https://doi.org/10.1016/j.matpr.2020.12.1157>.
19. Renuka, L.; Anantharaju, K.S.; Vidya, Y.S.; Nagaswarupa, H.P.; Prashantha, S.C.; Sharma, S.C.; Nagabhushana, H.; Darshan, G.P. A simple combustion method for the synthesis of multi-functional ZrO₂/CuO nanocomposites: Excellent performance as Sunlight photocatalysts and enhanced latent fingerprint detection. *Appl. Catal. B Environ.* **2017**, *210*, 97–115. <https://doi.org/10.1016/j.apcatb.2017.03.055>.
20. Kang, W.; Guo, H.; Varma, A. Noble-metal-free NiCu/CeO₂ catalysts for H₂ generation from hydrous hydrazine. *Appl. Catal. B Environ.* **2019**, *249*, 54–62. <https://doi.org/10.1016/j.apcatb.2019.02.066>.
21. Li, X.; Wu, J.; Pan, Y. Preparation of nanostructured Cu/Zr metal mixed oxides via self-sustained oxidation of a CuZr binary amorphous alloy. *J. Mater. Sci. Technol.* **2019**, *35*, 1601–1606. <https://doi.org/10.1016/j.jmst.2019.03.020>.
22. Dong, J.; Hou, Z.; Zhao, Q.; Yang, Q. Synthesis and Characterization of Nickel-doped Manganese Dioxide Electrode Materials for Supercapacitors. *E3S Web Conf.* **2019**, *79*, 03002. <https://doi.org/10.1051/e3sconf/20197903002>.
23. Jonkus, G.; Levinas, R.; Tsyntaru, N.; Cesiulis, H. Insights into the Electrochemical Synthesis and Supercapacitive Behaviour of 3D Copper Oxide-Based Nanostructures. *Solids* **2025**, *6*, 15. <https://doi.org/10.3390/solids6020015>.
24. Padmadevi, B.; Kalaivani, T. Facile synthesis of manganese-copper-zirconium mixed oxide nanocomposites: A potential electrode material for high performance supercapacitors. *Ceram. Int.* **2022**, *48*, 36101–36109. <https://doi.org/10.1016/j.ceramint.2022.08.152>.
25. Elmouwahidi, A.; Bailón-García, E.; Pérez-Cadenas, A.F.; Maldonado-Hódar, F.J.; Castelo-Quibén, J.; Carrasco-Marín, F. Electrochemical performances of supercapacitors from carbon-ZrO₂ composites. *Electrochim. Acta* **2018**, *259*, 803–814. <https://doi.org/10.1016/j.electacta.2017.11.041>.

26. Zenasni, M.; Belhadj, H.; Kiari, M.; Alelyani, M.; Alhailiy, A.B.; Benyoucef, A.; Bakkour, Y. Synthesis, characterization, and enhanced electrochemical behavior of polypyrrole doped $\text{ZrO}_2\text{-ZnO}$ electrode materials for supercapacitor applications. *Front. Energy Res.* **2023**, *11*, 1244699. <https://doi.org/10.3389/fenrg.2023.1244699>.
27. Nicolaescu, M.; Popescu, M.-I.; Codrean, C.; Hulka, I.; Orha, C.; Lazau, C.; Bandas, C.; Duteanu, N. Fabrication and performance evaluation of the NPC/amorphous- $\text{Sn}_2\text{P}_2\text{O}_7$ by dealloying of CuNiSnP alloy for supercapacitor application. *Sustain. Energy Technol. Assess.* **2025**, *80*, 104383. <https://doi.org/10.1016/j.seta.2025.104383>.
28. Shrivastav, V.; Mansi; Dubey, P.; Shrivastav, V.; Kaur, A.; Hołdyński, M.; Krawczyńska, A.; Tiwari, U.K.; Deep, A.; Nogala, W.; et al. Diffusion controlled electrochemical analysis of MoS_2 and MOF derived metal oxide–carbon hybrids for high performance supercapacitors. *Sci. Rep.* **2023**, *13*, 20675. <https://doi.org/10.1038/s41598-023-47730-4>.
29. Simon, P.; Gogotsi, Y. Materials for electrochemical capacitors. *Nat. Mater.* **2008**, *7*, 845–854. <https://doi.org/10.1038/nmat2297>.
30. Lv, S.; Zhang, Z.; Wang, R.; Wang, H.; Chu, X.; Yang, F.; Wang, S.; Wang, C. Hierarchical $\text{NiCo}_2\text{O}_4/\text{NiCoS}$ Nanoarrays for Improved Electrochemical Performance. *Materials* **2026**, *19*, 1419. <https://doi.org/10.3390/ma19071419>.
31. Anantharaj, S.; Noda, S. iR drop correction in electrocatalysis: Everything one needs to know! *J. Mater. Chem. A* **2022**, *10*, 9348–9354. <https://doi.org/10.1039/D2TA01393B>.
32. Thorat, J.P.; Nikam, R.P.; Lokhande, V.C.; Lokhande, C.D. Porous NiCo_2O_4 electrodes for high-energy asymmetric supercapacitor: Effect of annealing. *J. Mater. Sci.* **2023**, *58*, 9586–9604. <https://doi.org/10.1007/s10853-023-08602-4>.
33. Beyers, I.; Bensmann, A.; Hanke-Rauschenbach, R. Ragone plots revisited: A review of methodology and application across energy storage technologies. *J. Energy Storage* **2023**, *73*, 109097. <https://doi.org/10.1016/j.est.2023.109097>.
34. Ku, B.; Park, S.; Hwang, S.; Lim, S.; Yoon, W.-S.; Kim, J. From Materials to Systems: Challenges and Solutions for Fast-Charge/Discharge Na-Ion Batteries. *Adv. Energy Mater.* **2025**, e04664, early view. <https://doi.org/10.1002/aenm.202504664>.
35. Xiong, X.; Luo, W.; Hu, X.; Chen, C.; Qie, L.; Hou, D.; Huang, Y. Flexible Membranes of MoS_2/C Nanofibers by Electrospinning as Binder-Free Anodes for High-Performance Sodium-Ion Batteries. *Sci. Rep.* **2015**, *5*, 9254. <https://doi.org/10.1038/srep09254>.
36. Wang, H.; Fan, B.; Luo, Z.; Wu, Q.; Zhou, X.; Wang, F. A unique hierarchical structure: NiCo_2O_4 nanowire decorated NiO nanosheets as a carbon-free cathode for Li-O_2 battery. *Catal. Sci. Technol.* **2021**, *11*, 7632–7639. <https://doi.org/10.1039/D1CY01487K>.
37. Li, M.; Wei, J.; Ren, L.; Zhao, Y.; Shang, Z.; Zhou, D.; Liu, W.; Luo, L.; Sun, X. Superwetting behaviors at the interface between electrode and electrolyte. *Cell Rep. Phys. Sci.* **2021**, *2*, 100374. <https://doi.org/10.1016/j.xcrp.2021.100374>.
38. Guo, J.; Li, Y.; Meng, J.; Pedersen, K.; Gurevich, L.; Stroe, D.-I. Understanding the mechanism of capacity increase during early cycling of commercial NMC/graphite lithium-ion batteries. *J. Energy Chem.* **2022**, *74*, 34–44. <https://doi.org/10.1016/j.jechem.2022.07.005>.
39. Zhao, S.; Song, Z.; Qing, L.; Zhou, J.; Qiao, C. Surface Wettability Effect on Energy Density and Power Density of Supercapacitors. *J. Phys. Chem. C* **2022**, *126*, 9248–9256. <https://doi.org/10.1021/acs.jpcc.2c01455>.
40. Zequine, C.; Ranaweera, C.K.; Wang, Z.; Singh, S.; Tripathi, P.; Srivastava, O.N.; Gupta, B.K.; Ramasamy, K.; Kahol, P.K.; Dvornic, P.R.; et al. High Performance and Flexible Supercapacitors based on Carbonized Bamboo Fibers for Wide Temperature Applications. *Sci. Rep.* **2016**, *6*, 31704. <https://doi.org/10.1038/srep31704>.
41. Huang, H.-S.; Chang, K.-H.; Suzuki, N.; Yamauchi, Y.; Hu, C.-C.; Wu, K.C.W. Evaporation-Induced Coating of Hydrous Ruthenium Oxide on Mesoporous Silica Nanoparticles to Develop High-Performance Supercapacitors. *Small* **2013**, *9*, 2520–2526. <https://doi.org/10.1002/smll.201202786>.
42. Pal, A.; Das, T.; Ghosh, S.; Nandi, M. Supercapacitor behaviour of manganese dioxide decorated mesoporous silica synthesized by a rapid sol–gel inverse micelle method. *Dalton Trans.* **2020**, *49*, 12716–12730. <https://doi.org/10.1039/D0DT01237H>.
43. Joysi, M.G.; Senthil, S.; Jennifer, J.S.; Muthupandi, S.; Galeb, W.; AnnieCanisius, D.; Ruban, M.J.R.; Varghese, D.; Raj, M.V.A. Exploring ternary metal oxides $\text{MnO}_2/\text{CuO}/\text{ZrO}_2$ composites for supercapacitor applications. *Results Chem.* **2024**, *10*, 101682. <https://doi.org/10.1016/j.rechem.2024.101682>.
44. He, D.; Wang, G.; Liu, G.; Suo, H.; Zhao, C. Construction of leaf-like $\text{CuO-Cu}_2\text{O}$ nanocomposites on copper foam for high-performance supercapacitors. *Dalton Trans.* **2017**, *46*, 3318–3324. <https://doi.org/10.1039/C7DT00287D>.

45. Yin, Z.; Wang, X.; Song, M.; Wu, Z.; Li, Z.; Wang, X.; Zhu, M.; Liu, D.; Zhao, J. Facile fabrication of Cu₂O/Cu columnar array electrode through dealloying and in situ oxidation for supercapacitor applications. *J. Solid State Electrochem.* **2020**, *24*, 1313–1324. <https://doi.org/10.1007/s10008-020-04632-z>.
46. Morariu, M.-I.; Nicolaescu, M.; Hulka, I.; Duțeanu, N.; Orha, C.; Lăzău, C.; Bandas, C. Fabrication of Cu₂O/CuO Nanowires by One-Step Thermal Oxidation of Flexible Copper Mesh for Supercapacitor Applications. *Batteries* **2024**, *10*, 246. <https://doi.org/10.3390/batteries10070246>.

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.