

BINARY TRANSITION METAL OXIDE AS ADVANCED ENERGY STORAGE MATERIALS

Abstract

Binary transition metal oxides (BTMOs) have received a lot of attention as potential new electrode materials for supercapacitors because of their improved structural stability, larger reversible capacity, and higher electronic conductivity. Energy storage technologies have emerged as the leading contenders for the next wave of electrochemical applications in recent years. This chapter includes a thorough explanation of BTMO materials as well as the most popular synthetic techniques. In addition; we analyze a number of prominent BTMOs and their composites for use with supercapacitors. Furthermore, in this exciting area to make considerable progress in future supercapacitor applications are discussed.

Keywords: BTMOs and BTMO nanocomposites, Metal Oxide, supercapacitor.

Authors

M. Priyadharshan

Department of Chemistry
Periyar Maniammai Institute of Science and Technology (Deemed to be University)
Vallam, Thanjavur, Tamil Nadu, India.

M. Karthikeyan

Department of Chemistry
Periyar Maniammai Institute of Science and Technology (Deemed to be University)
Vallam, Thanjavur, Tamil Nadu, India.

A. Manohar

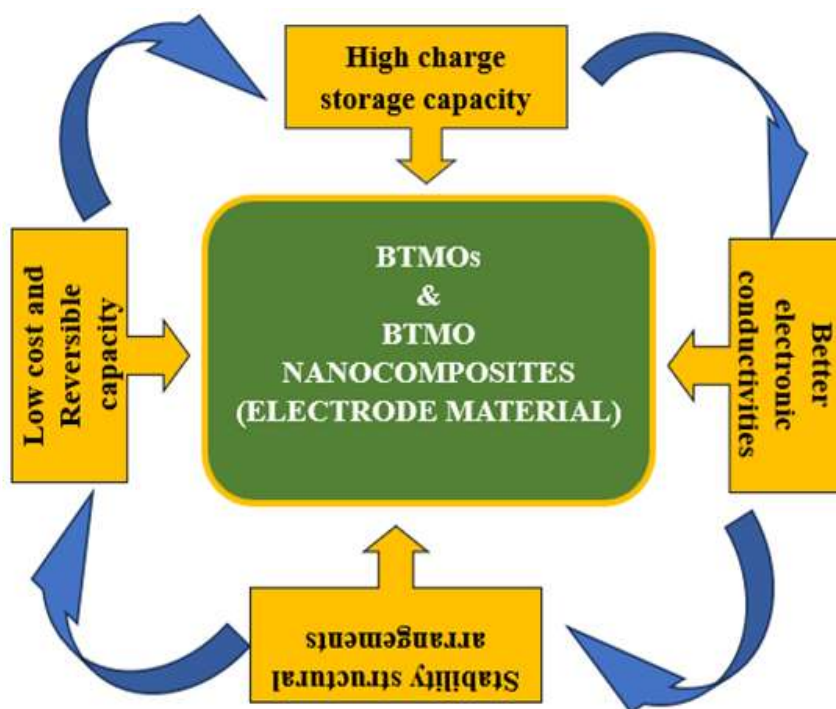
Department of Chemistry
Periyar Maniammai Institute of Science and Technology (Deemed to be University)
Vallam, Thanjavur, Tamil Nadu, India.

A. Akalya

Department of Chemistry
Periyar Maniammai Institute of Science and Technology (Deemed to be University)
Vallam, Thanjavur, Tamil Nadu, India.

I. INTRODUCTION

Energy storage is becoming more crucial than ever before due to the fast-growing interest in portable energy gadgets. Binary transition metal oxides (BTMOs) have received a great deal of attention as potential new energy storage materials because of their superior structural stability, improved electronic conductivity, and larger reversible capacity.[1] Numerous studies have been conducted in recent years to investigate and develop flexible energy storage systems, with the main objective of applying flexible electronics to devices like flexible displays, portable electronics, electronic sensors, power backup, mobile phones, laptops, and other items. The majority of the existing markets for rechargeable energy storage are dominated by the design and production of electrochemical energy storage systems with high flexibility, high energy densities, and high-power densities. [2] Because of their quick charge-discharge rates, high power density, and exceptional cyclability, supercapacitors (SCs) are the most promising and quickly developing storage device for a variety of applications.[3] In order to partially replace fossil fuels, significant efforts have been undertaken over the past 10 years to harness renewable energy sources like thermal, solar, wind, and tidal energy. The widespread use of these alternating renewable energy sources must be accomplished with the help of capable energy storage systems.[4][5][6] Supercapacitors have attracted a lot of interest due to their rapid charge and discharge speeds, reversibility, safety, prolonged cycle life, high power density, and environmental friendliness.[7] Supercapacitors have advantages over other energy storage technologies, including long life cycles, quick charging and discharging, high power density, quick charge storage, and high energy density. These qualities make supercapacitors a complement to fuel cells, traditional rechargeable batteries, and capacitors.[8] Electrical double-layer capacitors (EDLCs) and pseudo capacitors resulting from various energy storage techniques can be found under the category of supercapacitors. The EDLCs store charges by electrostatic adsorption/desorption at the interface of the electrodes/electrolytes. Due to their large specific surface area and excellent conductivity, carbon nanotubes (CNTs), graphene, carbon aerogels, and activated carbon are frequently employed in EDLCs.[9] Researchers looking to create devices with high power output, a long lifetime, and a fast-charging time have been interested in developing sustainable electrochemical energy conversion and storage solutions to fulfil the rising need for power in daily life.[10] Due to its capacity to enhance redox chemistry, BTMOs have attracted a great deal of interest for the advancement of Supercapacitors like [3] Since binary metal oxides have a high theoretical specific capacitance, they have received a lot of attention as supercapacitor electrode materials such as ZnFe₂O₄/rGO composite, [11] NiCo₂O₄, [12] CoV₂O₆, [13] BiVO₄/PANI composite [14] and NiCo₂S₄. [15]. BTMOs typically have higher specific surface areas, a different redox potential, and superior electrical conductivity when compared to single transition metal oxides, these characteristics are advantageous for achieving good electrochemical performance. [16,17,18]. Due to their superior conductivity and large surface areas, investigations recently have concentrated on using binary metal oxide materials or binary metal oxide nanocomposites as electrode materials for supercapacitor applications are shown in figure 1. There are numerous ways to make binary metal oxides, including hydrothermal, solvothermal, microwave-assisted, ultrasonication, and green technology. Among these options, the majority of BTMOs or BTMOs nanocomposites for capacitors have been made by precipitation using chemical oxidation and thermal reaction processes. Here in we present the most recent developments in the study of BTMOs and BTMOs nanocomposites for electrochemical supercapacitor electrodes.



Properties of BTMOs and BTMOs/Nanocomposite as electrode material

II. SYNTHESIS METHODS

The BTMOs and BTMO nanocomposites can be prepared by different methods such as hydrothermal [19], Co-precipitation [20], Sol-gel [21], Spray pyrolysis [22] and greensynthesis [23]. Out of all the ways stated above, the hydro thermal approach is a special technique for quickly creating metal oxide nanostructures with controlled shape, high purity, and superior crystalline nanoparticles [20].

- 1. Hydrothermal Method:** Highly crystalline and phase-pure BTMO nanostructures, which are challenging to produce by high-temperature solid-state processes, have been demonstrated to be easily and successfully synthesized using the hydrothermal approach [24,25]. Continuous flow hydrothermal synthesis, which has primarily been used with materials based on metal oxide, provides a low-cost, environmentally friendly, and highly scalable method for the production of inorganic nanomaterials [26]. The use of this simple microwave hydrothermal technique to create BTMO nanocomposites for supercapacitor electrodes has, however, received relatively little attention in the literature [11].
- 2. Co-precipitation Method:** The most popular technique, for making binary metal oxides is easy and inexpensive [21]. Diverse techniques are used to create binary metal oxides. Unfortunately, either their poor electrochemical characteristics or technical difficulties limit these binary transition metal oxides. The complex synthetic process restricts the practical use of supercapacitors, thus it's important to provide a simple and effective method to hasten the material preparation cycle for mass production. The simple method of chemical co-precipitation for producing CoV_2O_6 , a high-performance binary transition metal oxide. To complete the material synthesis in this process, simple time- and energy-saving techniques have been created [27]. The method is comparatively easy to use, and

setup is not too difficult. The inability to scale up for mass production is thus one of the major limitations of the traditional coprecipitation synthesis process. It becomes more challenging to ensure uniformity as the reaction volume increases [28,29].

- 3. Sol-gel Method:** Sol-gel chemistry frequently provides a simple wet-chemical synthesis approach to produce size- and shape-controlled nanostructures by hydrolyzing and condensing molecular precursors into polymeric oxide networks. The sol-gel process has substantially improved and been used to create solid materials with exceptional electrical, optical, magnetic, thermal, and mechanical properties, such as inorganic oxides, organosilica and organic-inorganic hybrids [30,31,32,33]. Recent research recommended the more beneficial sol-gel synthesis method, which uses environmentally friendly water as a solvent and involves less expensive strategies [34]. Sol-gel synthesis is one of the most straightforward techniques for producing high-quality nano and microstructures. Compared to previous synthesis techniques, this method has a number of advantages, such as the ability to regulate the texture, size, and surface features of the materials, ease of use, affordability, superior quality, and the ability to create materials with a large surface area [35].
- 4. Spray Pyrolysis:** Flame spray pyrolysis (FSP), which offers benefits in terms of flexibility, speed, and scalability, is a possible substitute approach to manufacture methanol synthesis catalysts [36]. Simple metal oxides like TiO_2 , Al_2O_3 , and SiO_2 were the only ones that could be produced with this dry synthetic process for a very long time despite its benefits of high purity and continuous synthesis at high rates. Since its creation a decade ago, the technology in this family known as "flame spray pyrolysis" (FSP) has become incredibly adaptable [37]. One of the potential methods for producing different oxide materials quickly and sequentially, from simple to complex components, is flame spray pyrolysis. But FSP frequently produced micron-scale particles with a wide size distribution because the flame's inhomogeneous temperature profile causes varying degrees of aggregation and the agglomeration of primary particles [38].
- 5. Green Synthesis:** In green technique, Phytocompounds are said to function as reducing and stabilizing agents for the synthesis of nanomaterials when the process is supported by plants. They are added to the synthetic material as stabilizing agents to stabilize the nanoparticles and stop them from clumping together [39]. Because bioactive chemicals bind metal oxide to form nanoparticles; the biosynthetic process is simple and economical. Significant research has been done on using plant extract to make different metal oxide nanoparticles [40]. In these greener solutions, the metal ions are converted into nanoparticles using components from living organisms like plants, bacteria, fungi, algae, and lichens. Due of their accessibility, affordability, and environmental friendliness, plants are favored among these over physical and chemical techniques [41].

III. BINARY TRANSITIONAL METAL OXIDE AS ELECTRODE MATERIAL

Pseudo-capacitive transition metal oxides (Ni, Co, Fe, Mn, etc.) are extensively researched due to their high theoretical capacitances, low cost, and reversible faradaic redox reactions, which result in higher specific capacitances compared to carbonaceous materials based on an electrical double-layer charge storage mechanism [42]. Researchers have become interested in binary/ternary oxides of transition metals because of its superior electrochemical capabilities, improved conductivity values, and excellent structural stability. In particular,

binary-oxide of third-dimensional transition metals, which possess spinel structure with formula $AxB_{3-x}O_4$, where 'A' and 'B' can be assigned to any two transition metals, such as Cu, Mn, Ni, Co, Zn, Fe, etc [14]. There are various techniques to synthesize the BTMOs as electrode material for supercapacitor application is mentioned below table.

Various Synthesis Techniques of BTMOs and its Properties with Application

BTMOs Electrode material	Synthesized methods	Application	Advantages	References
CoV_2O_6	Coprecipitation method	Supercapacitor / Energy storage	High stability, high current density, better electrochemical performance	[28]
$BiVO_4/PANI$	Hydrothermal method	Supercapacitor / Energy storage	Novel electrode material, High current density, high capacitance	[14]
$Zn_3V_2O_8$	Wet chemical method	Supercapacitor / Energy storage	Enhanced electrochemical performance material, numerous electrochemical active sites	[43]
$FeCo_2O_4/PANI$	Hydrothermal route	Supercapacitor / Energy storage	Exclusive color morphology, outstanding supercapacitive performance	[44]
$ZnMn_2O_4$	Hydrothermal route	Supercapacitor / Energy storage	Promising material for high energy storage, high specific capacitance	[45]

Binary metal oxides, however, can integrate the contributions from two different types of ions and therefore provide richer redox chemical ability as compared to single-component oxides. As a result, BTMOs and their composites have generated a lot of attention in supercapacitor applications [1].

IV. CONCLUSION

In this chapter, we have laid out the traditional approaches and most recent developments in using binary metal oxides as supercapacitor energy storage materials. There

are still a lot of challenges in synthetically fabricating BTMOs that completely meet the needs of certain applications. In synthetic processes, it is still relatively difficult to produce BTMOs that satisfy all the requirements of a certain application using a simple procedure. The electrochemical performance of BTMOs can still be improved, however high specific capacitance and extended cycle stability remain obstacles. BTMOs exhibit strong charge-storage capabilities, improved electrical conductivities, and structural stability. Due to these qualities, they are strong contenders to serve as the electrode material for supercapacitors. However, we look forward to encouraging further study in this fascinating field in order to make significant advancements in supercapacitor applications in the future.

REFERENCES

- [1] Zhang, Y. *et al.* (2015) 'Binary metal oxide: Advanced Energy Storage Materials in Supercapacitors', *Journal of Materials Chemistry A*, 3(1), pp. 43–59. doi:10.1039/c4ta04996a.
- [2] Muralee Gopi, C.V.V. *et al.* (2020) 'recent progress of Advanced Energy Storage Materials for flexible and wearable supercapacitor: From design and development to applications', *Journal of Energy Storage*, 27, p. 101035. Doi: 10.1016/j.est.2019.101035.
- [3] Kumar, Y.A., Kumar, K.D. and Kim, H.-J. (2020) 'Reagents assisted ZnCo₂O₄ nanomaterial for supercapacitor application', *Electrochimica Acta*, 330, p. 135261. doi: 10.1016/j.electacta.2019.135261.
- [4] Suresh Babu, R. *et al.* (2019) 'Asymmetric supercapacitor based on carbon nanofibers as the anode and two-dimensional copper cobalt oxide nanosheets as the cathode', *Chemical Engineering Journal*, 366, pp. 390–403. doi: 10.1016/j.cej.2019.02.108.
- [5] Aricò, A.S. *et al.* (2005) 'Nanostructured materials for advanced energy conversion and storage devices', *Nature Materials*, 4(5), pp. 366–377. doi:10.1038/nmat1368.
- [6] Simon, P. and Gogotsi, Y. (2008) 'Materials for electrochemical capacitors', *Nature Materials*, 7(11), pp. 845–854. doi:10.1038/nmat2297.
- [7] Kumar, Y.A. *et al.* (2022) 'Self-supported co₃o₄@mo-co₃o₄ needle-like nanosheet heterostructured architectures of battery-type electrodes for high-performance asymmetric supercapacitors', *Nanomaterials*, 12(14), p. 2330. doi:10.3390/nano12142330.
- [8] Askari, M.B. *et al.* (2022) 'MnCo₂O₄/NiCo₂O₄/RGO as a catalyst based on binary transition metal oxide for the methanol oxidation reaction', *Nanomaterials*, 12(22), p. 4072. doi:10.3390/nano12224072.
- [9] Burt, R., Birkett, G. and Zhao, X.S. (2014) 'A review of molecular modelling of electric double layer capacitors', *Physical Chemistry Chemical Physics*, 16(14), p. 6519. doi:10.1039/c3cp55186e.
- [10] Shinde, S.K. *et al.* (2019) 'Novel approach to synthesize NiCo₂S₄ composite for high-performance supercapacitor application with different molar ratio of Ni and Co', *Scientific Reports*, 9(1). doi:10.1038/s41598-019-50165-5.
- [11] Mo, X. *et al.* (2023) 'A facile microwave hydrothermal synthesis of ZnFe₂O₄/RGO nanocomposites for supercapacitor electrodes', *Nanomaterials*, 13(6), p. 1034. doi:10.3390/nano13061034.
- [12] Yedluri, A.K. and Kim, H.-J. (2020) 'Correction: Enhanced electrochemical performance of nanoplate Nickel Cobaltite (NiCo₂O₄) supercapacitor applications', *RSC Advances*, 10(3), pp. 1296–1296. doi:10.1039/c9ra90096a.
- [13] He, X. *et al.* (2019) 'A facile method to synthesize CoV₂O₆ as a high-performance supercapacitor cathode', *RSC Advances*, 9(17), pp. 9475–9479. doi:10.1039/c8ra10041a.
- [14] Srinivasan, R. *et al.* (2020) 'Study on the electrochemical behavior of bivo₄/pani composite as a high-performance supercapacitor material with excellent cyclic stability', *Journal of Electroanalytical Chemistry*, 861, p. 113972. doi:10.1016/j.jelechem.2020.113972.
- [15] Gao, Y.-P. and Huang, K.-J. (2017) 'NiCo₂S₄ materials for supercapacitor applications', *Chemistry - An Asian Journal*, 12(16), pp. 1969–1984. doi:10.1002/asia.201700461.
- [16] Zheng, J.H. *et al.* (2019) 'Binary transition metal oxides (BTMO) (Co-Zn, co-cu) synthesis and high supercapacitor performance', *Journal of Alloys and Compounds*, 772, pp. 359–365. doi:10.1016/j.jallcom.2018.09.067.
- [17] Nagarani, S. *et al.* (2018) 'Synthesis and characterization of binary transition metal oxide/reduced graphene oxide nanocomposites and its enhanced electrochemical properties for supercapacitor applications', *Journal of Materials Science: Materials in Electronics*, 29(14), pp. 11738–11748. doi:10.1007/s10854-018-9272-0.

- [18] Yang, S. *et al.* (2018) ‘Controllable ZnFe₂O₄/reduced graphene oxide hybrid for high-performance supercapacitor electrode’, *Electrochimica Acta*, 268, pp. 20–26. doi:10.1016/j.electacta.2018.02.028.
- [19] Priya, M. *et al.* (2019) ‘Structural and electrochemical properties of znco₂o₄ nanoparticles synthesized by hydrothermal method’, *Vacuum*, 167, pp. 307–312. doi:10.1016/j.vacuum.2019.06.020.
- [20] Vijayanand, S. *et al.* (2011) ‘Nanostructured spinel znco₂o₄ for the detection of LPG’, *Sensors and Actuators B: Chemical*, 152(1), pp. 121–129. doi:10.1016/j.snb.2010.09.001.
- [21] Wei, X., Chen, D. and Tang, W. (2007) ‘Preparation and characterization of the spinel oxide ZnCo₂O₄ obtained by Sol–Gel Method’, *Materials Chemistry and Physics*, 103(1), pp. 54–58. doi:10.1016/j.matchemphys.2007.01.006.
- [22] Choi, S.H. and Kang, Y.C. (2013) ‘Yolk-shell, hollow, and single-crystalline znco₂o₄powders: Preparation using a simple one-pot process and application in lithium-ion batteries’, *ChemSusChem*, 6(11), pp. 2111–2116. doi:10.1002/cssc.201300300.
- [23] Mayedwa, N. *et al.* (2021) ‘Biosynthesis and characterization of multifunctional mixed oxides of ZnCr₂O₄/ZnCrO₄ nanoparticulate from natural leaf extracts of hibiscus Rosa sinensis’, *Materials Today: Proceedings*, 36, pp. 309–312. doi:10.1016/j.matpr.2020.04.108.
- [24] Baruah, S. and Dutta, J. (2011) ‘Zinc stannate nanostructures: Hydrothermal synthesis’, *Science and Technology of Advanced Materials*, 12(1), p. 013004. doi:10.1088/1468-6996/12/1/013004.
- [25] Dinesh, M., Haldorai, Y. and Rajendra Kumar, R.T. (2020) ‘Mn–Ni binary metal oxide for high-performance supercapacitor and electro-catalyst for oxygen evolution reaction’, *Ceramics International*, 46(18), pp. 28006–28012. doi:10.1016/j.ceramint.2020.07.295.
- [26] Dunne, P.W. *et al.* (2014) ‘The rapid size- and shape-controlled continuous hydrothermal synthesis of metal sulphide nanomaterials’, *Nanoscale*, 6(4), pp. 2406–2418. doi:10.1039/c3nr05749f.
- [27] He, X. *et al.* (2019) ‘A facile method to synthesize CoV₂O₆ as a high-performance supercapacitor cathode’, *RSC Advances*, 9(17), pp. 9475–9479. doi:10.1039/c8ra10041a.
- [28] James, M. *et al.* (2020) ‘Microfluidic synthesis of iron oxide nanoparticles’, *Nanomaterials*, 10(11), p. 2113. doi:10.3390/nano10112113.
- [29] Li, Z. *et al.* (2008) ‘Direct coprecipitation route to monodisperse dual-functionalized magnetic iron oxide nanocrystals without size selection’, *Small*, 4(2), pp. 231–239. doi:10.1002/sml.200700575.
- [30] Yarbrough, R. *et al.* (2020) ‘A sol–gel synthesis to prepare size and shape-controlled mesoporous nanostructures of binary (ii–VI) metal oxides’, *RSC Advances*, 10(24), pp. 14134–14146. doi:10.1039/d0ra01778g.
- [31] Rathnayake, H. *et al.* (2012) ‘Perylenediimide functionalized bridged-siloxane nanoparticles for bulk heterojunction organic photovoltaics’, *Nanoscale*, 4(15), p. 4631. doi:10.1039/c2nr30538k.
- [32] Zhan, Z. and Zeng, H.C. (1999) ‘A catalyst-free approach for sol–gel synthesis of highly mixed zro₂–sio₂ oxides’, *Journal of Non-Crystalline Solids*, 243(1), pp. 26–38. doi:10.1016/s0022-3093(98)00810-2.
- [33] Sui, R. and Charpentier, P. (2012) ‘Synthesis of metal oxide nanostructures by direct sol–gel chemistry in supercritical fluids’, *Chemical Reviews*, 112(6), pp. 3057–3082. doi:10.1021/cr2000465.
- [34] Abebe, B., Zereffa, E.A. and Murthy, H.C. (2020) ‘Synthesis of poly (vinyl alcohol)-aided ZnO/Mn₂O₃ nanocomposites for acid orange-8 dye degradation: Mechanism and antibacterial activity’, *ACS Omega*, 6(1), pp. 954–964. doi:10.1021/acsomega.0c05597.
- [35] Navas, D. *et al.* (2021) ‘Review on sol-gel synthesis of perovskite and oxide nanomaterials’, *Gels*, 7(4), p. 275. doi:10.3390/gels7040275.
- [36] Zhu, J. *et al.* (2021) ‘Flame synthesis of Cu/ZnO–CEO₂ catalysts: Synergistic metal–support interactions promote CH₃oh selectivity in CO₂ hydrogenation’, *ACS Catalysis*, 11(8), pp. 4880–4892. doi:10.1021/acscatal.1c00131.
- [37] Pokhrel, S., Nel, A.E. and Mädler, L. (2012) ‘Custom-designed nanomaterial libraries for testing metal oxide toxicity’, *Accounts of Chemical Research*, 46(3), pp. 632–641. doi:10.1021/ar300032q.
- [38] Khan, S. *et al.* (2020) ‘Control of particle size in flame spray pyrolysis of TB–doped Y₂O₃ for bio-imaging’, *Materials*, 13(13), p. 2987. doi:10.3390/ma13132987.
- [39] Shaheen, I. *et al.* (2020) ‘Green synthesis of zno–CO₃O₄ nanocomposite using facile foliar fuel and investigation of its electrochemical behaviour for supercapacitors’, *New Journal of Chemistry*, 44(42), pp. 18281–18292. doi:10.1039/d0nj03430d.
- [40] Mayedwa, N. *et al.* (2018) ‘Green synthesis of Zin Tin Oxide (znsno₃) nanoparticles using Aspalathus linearis natural extracts: Structural, morphological, optical and Electrochemistry Study’, *Applied Surface Science*, 446, pp. 250–257. doi:10.1016/j.apsusc.2017.12.161.
- [41] Alavi, M. and Varma, R.S. (2021) ‘Phytosynthesis and modification of metal and metal oxide nanoparticles/nanocomposites for antibacterial and anticancer activities: Recent advances’, *Sustainable Chemistry and Pharmacy*, 21, p. 100412. doi: 10.1016/j.scp.2021.100412.

- [42] Shaheen, N. *et al.* (2021) 'Fabrication of different conductive matrix supported binary metal oxides for supercapacitors applications', *Ceramics International*, 47(4), pp. 5273–5285. doi: 10.1016/j.ceramint.2020.10.108.
- [43] Shaheen, N. *et al.* (2021) 'Fabrication of different conductive matrix supported binary metal oxides for supercapacitors applications', *Ceramics International*, 47(4), pp. 5273–5285. doi: 10.1016/j.ceramint.2020.10.108.
- [44] Rajkumar, S. *et al.* (2021) 'Enhanced electrochemical behaviour of FeCo₂O₄/pani electrode material for supercapacitors', *Journal of Alloys and Compounds*, 874, p. 159876. doi: 10.1016/j.jallcom.2021.159876.
- [45] Senthilkumar, N. *et al.* (2019) 'Studies on electrochemical properties of heterolite (ZnMn₂O₄) nanostructure for Supercapacitor Application', *Physica E: Low-dimensional Systems and Nanostructures*, 106, pp. 121–126. doi:10.1016/j.physe.2018.10.027.