

Article

Microwave Synthesis of MnO₂-Lignin Composite Electrodes for Supercapacitors

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Abstract: The demand for energy storage devices made from biodegradable materials has increased significantly due to sustainability. Currently, such devices possess vital issues, such as high manufacturing costs and toxicity, low reliability, as well as poor electrochemical performance. In this research, microwave synthesis was conducted to fabricate a low-cost, high-performing, plant-based electroactive material. MnO₂ microparticles fabricated via microwave irradiation were deposited on two plant-based materials as substrates made of Al/lignin and Al/AC/lignin. The quasi-solid-state supercapacitors were assembled using a polymeric gel electrolyte of PVA/H₃PO₄. Scanning electron microscopy was performed to examine the polydispersity, morphology, and porosity of the micro-MnO₂ deposited materials. FTIR and UV-vis spectroscopy were performed to study the composition and verify deposition of micro-MnO₂ on the lignin-based matrixes. Cyclic voltammetry (CV) was employed to study the polarization resistance of the system. The cyclic charge-discharge (CCD) and electrochemical impedance spectroscopy (EIS) were performed to observe cyclic performance and interfacial resistances. Electrochemical tests showed that after 700 cycles of charge-discharge, both the supercapacitors exhibited high capacitance retention above 90%. Compared to the existing technology, this method enables consistent material structurization with tunable properties due to the controlled heating time and exposure to radiation with minimal waste. This work provides an alternative approach to synthesize low-cost and scalable green composite electrodes for flexible supercapacitors.

Keywords: green materials; polymers; composites; electrodes; microwave synthesis; clean energy; supercapacitors



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1. Introduction

The advancement in energy storage demands innovation for sustainability. The rapid technological development of consumer electronics with multiple applications has motivated research to develop high-performing, flexible, and eco-friendly energy storage devices [1–10]. These electrochemical devices are categorized as supercapacitors, batteries, and fuel cells. Supercapacitors are high-power-density storage systems with the ability to rapidly charge-discharge in an extended lifecycle [11–13]. Owing to this, supercapacitors have wide applications in industry, healthcare, and our daily life [14]. However, due to their low energy densities, their applications are restricted.

Many electronic devices manufactured today use hazardous materials that pose a risk to the environment. To avoid the detrimental impacts of spent energy storage systems, they must be processed and properly disposed of. The presence of toxic materials poses a major challenge in the disposal of these systems [15]. With an increasing demand for mobile computing and portable electronics, eco-friendly and biodegradable energy storage devices are of vital importance. For this purpose, green materials such as carbon-based electroactive materials and biomaterials are being considered. These materials are cost-effective, have

an adaptable morphology, and are biodegradable, making them excellent candidates. Lignin, an abundantly available biomaterial, is acquired as a waste product from the paper and pulping industries [16]. The porous structure and defects present in lignin make it a favorable candidate for use as an electroactive material [17,18]. In order to improve the performance of lignin, it has been doped with transition metal oxides, conduction polymers, and other carbonaceous materials [19]. Lignin has been used as a precursor to developing hierarchical porous carbons as electrode materials. Transition metal oxides (TMOs) such as NiO, RuO₂, Co₂O₃, and MnO₂ have been incorporated into the matrix of lignin. This has proven to be a successful method to boost the capacitive performance of the supercapacitor [20–22]. Owing to its synergistic behavior, ideal capacitive behavior, abundant availability, and low cost, MnO₂ is considered the most favorable candidate to improve the electrochemical performance of lignin [11,23].

Efficient charging/discharging requires electroactive materials with designated pores to increase the surface area. The reduced time of fabrication, enabling rapid nucleation and deep penetration, make microwave irradiation an attractive option to make electrode materials. Due to those characteristics, structural uniformity of metal oxides has been achieved [24]. However, few studies have performed microwave irradiation for the synthesis of MnO₂ particles. In addition, most of these methods are coupled with the template method or with hydrothermal conditions. The specific effect of microwave irradiation cannot be examined clearly when coupled with hydrothermal conditions. This is because the reaction conditions of the additional hydrothermal method alter the kinetics of crystal growth. For instance, Wang et al. used an ultrasound-microwave method for polymer P123 and acetylene black for a supercapacitor electrode [25]. The distinct advantage of microwaves on electrode properties could not be deciphered. Similarly, Liu et al. used a potassium-based catalyst and microwave radiation to make electrodes using corn straw [26]. This method creates a problem of catalyst poisoning and environmental disposal issues. Seong et al. used a potassium citrate-based synthesis method that utilized microwave radiation to obtain a hierarchical porous carbon electrode. Not only was the process expensive but also the chemicals used pose health hazards to humans [27]. Moreover, the effect of microwaves on the pseudo-capacitance could not be established. There is no report about decorating lignin with MnO₂ microparticles. It is necessary to understand the surface morphology, composition, and electrochemical performance of the MnO₂ particles fabricated via microwave synthesis deposited on green materials.

In this research, microwave irradiation was used to synthesize micro-MnO₂ particles, which were then deposited onto the lignin matrix via hydrothermal treatment. A solid-state asymmetric supercapacitor with an AC-Lig-MnO₂ composite electrode as an anode was fabricated. SEM was performed to study morphology, porosity, and polydispersity of the lignin-based matrix. Cyclic voltammetry (CV) was employed to study the polarization resistance of the system. The cyclic charge-discharge (CCD) and electrochemical impedance spectroscopy (EIS) were performed to observe cyclic performance and interfacial resistances. This work provides new insights into the synthesis of low-cost and scalable plant-based flexible supercapacitors.

2. Materials and Methods

2.1. Microwave-Irradiated Green Composite Electrode Preparation

To fabricate the green composite AC/Lig-MnO₂ electrode, 1 g of AC (Sigma Aldrich MW = 12.01 g mol^{−1}) was mixed with 0.5 g of alkali lignin (TCI) powder and DI water. This solution was then sonicated for 5 min. To prepare the MnO₂ particles, 22.2 mmol of 37% HCl (Sigma Aldrich, MW = 36.46 g mol^{−1}, density = 1.2 g mL^{−1}) was added to 5.5 mmol of KMnO₄ purchased from Sigma Aldrich (99%, MW = 158.03 g mol^{−1}, density = 2.7 g mL^{−1}). This solution was then placed in a 1000 W microwave for 4 min. The AC/Lignin solution was then mixed with the microwaved KMnO₄ solution and stirred magnetically for 15 min. After hydrothermal treatment at 160 °C for 1 h, the solution was centrifuged, washed with ethanol and DI water, and dried overnight. The final powder obtained was mixed with

NMP (Sigma Aldrich, MW = 99.13 g mol⁻¹, density = 1.028 g mL⁻¹, ≥99%) and PVDF (Sigma Aldrich, MW = 275,000 by GPC) to form a slurry, which was then coated on an Al foil (thickness = 0.98 mm) and dried in a vacuum furnace at 100 °C for 4 h. The substrate was cut in a circular plate with a diameter of 4 cm. The supercapacitor's interface thickness was 100 µm. The green composite Lig-MnO₂ electrode was fabricated in a similar manner. The schematic for the preparation method is shown in Figure 1.

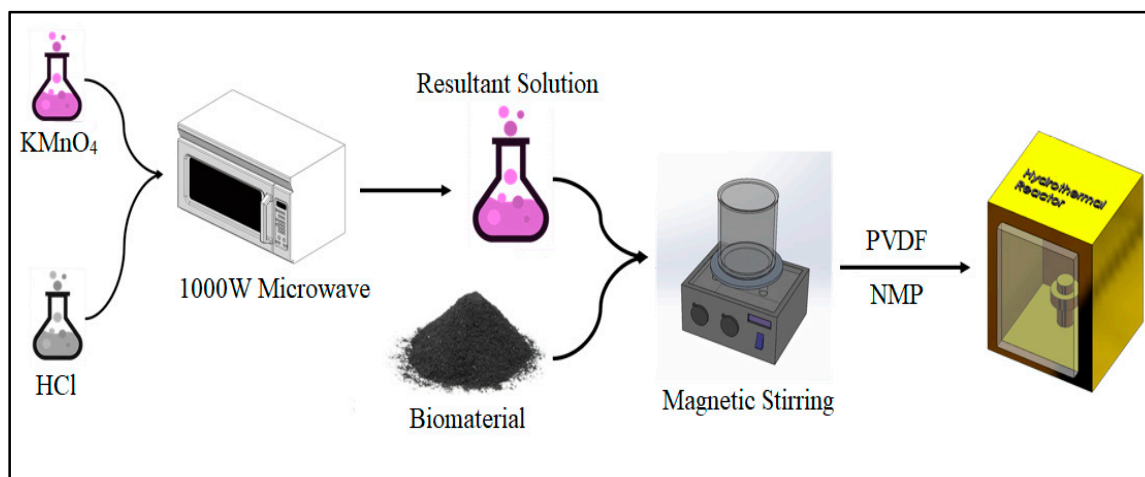


Figure 1. Schematic for the preparation of the electroactive materials.

2.2. Preparation of PVA/H₃PO₄ Gel Electrolyte

The gel electrolyte was prepared in a similar method as in our previous work [22].

2.3. Materials' Characterization

The scanning electron microscopy was performed using a VEGA/TESCAN SEM, using an SE detector at scanning voltage of 5 kV and magnification of 300×. The elemental composition analysis was performed using an Oxford EDS detector on FEI Quanta 600 SEM, and results were investigated using AZtec software offered by Oxford Instruments. EDS mapping was performed at 20 kV acceleration voltage. For XRD, we employed a Bruker D8 Advanced Powder Diffractometer. FTIR was performed using a Shimadzu FTIR Spectrophotometer IR Affinity-1, while UV spectroscopy was performed using a Shimadzu UV-2450 Spectrophotometer.

3. Results and Discussion

3.1. Materials' Characterization

3.1.1. Scanning Electron Microscope (SEM)

SEM analysis was performed to gauge the electrode surface and particle distribution. Figure 2a shows the uniform distribution of electroactive AC/Lig-MnO₂ (Figure 2a) and Lig-MnO₂ (Figure 2c) on the electrode surface. Micron-size MnO₂ particles can be seen embedded in the AC/lignin (Figure 2a) and lignin (Figure 2c) matrices. The electrode surfaces appear intact without any sign of wear or damage. This is important for good contact with the electrolyte and ensuring smooth charge transfer. In Figure 2b, the supercapacitor interface can be seen. The quasi-solid gel electrolyte can be seen placed between the outer Al electrodes. The interface appears mechanically stable and intact. The interface thickness is about 0.1 mm. A stable interface helps with the consistent performance of the supercapacitor.

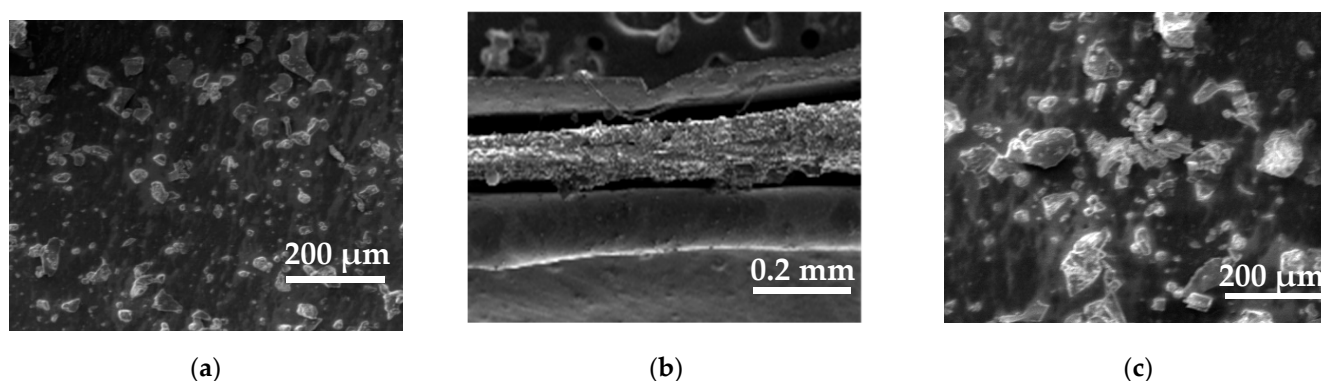


Figure 2. SEM images of (a) AC/Lig-MnO₂, (b) the supercapacitor interface, and (c) Lig-MnO₂.

3.1.2. FTIR Spectroscopy

The FTIR spectra are shown for both the composite electrodes in Figure 3. Peaks 1 and 2 at 526 and 536 cm^{-1} represent the Mn-O bond stretch. This demonstrates the successful deposition of micro-MnO₂ particles on the lignin and AC/lignin matrices [28]. Peak 3 at 1031.79 and peak 4 at 1257.36 correspond with O-H bending vibrations bonded with Mn atoms [29]. The peaks at 1614.15 (on the purple line) and 1720.19 (on the green line) correspond to the C=C bond stretch, indicating the presence of aromatic rings [22,30]. The presence of OH bonds indicates absorbed molecules of water in the MnO₂ structure. These water molecules enhance the diffusion of ions and improve the overall capacitance performance of the materials [31,32].

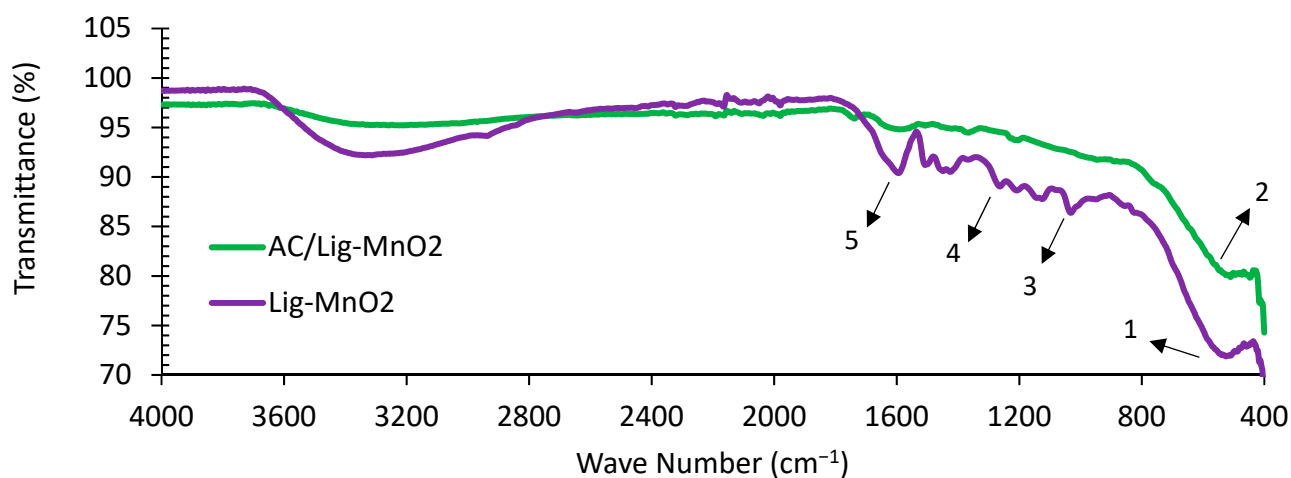


Figure 3. FTIR spectroscopy of AC/Lig-MnO₂ and Lig-MnO₂.

3.1.3. UV-Vis Spectroscopy

The UV-vis spectroscopy is shown for both the composite electrodes in Figure 4. A characteristic broad peak of absorption can be seen in the range 300–350 nm [21]. This confirms the successful deposition of the micro-MnO₂ particles onto the lignin and AC/lignin matrices.

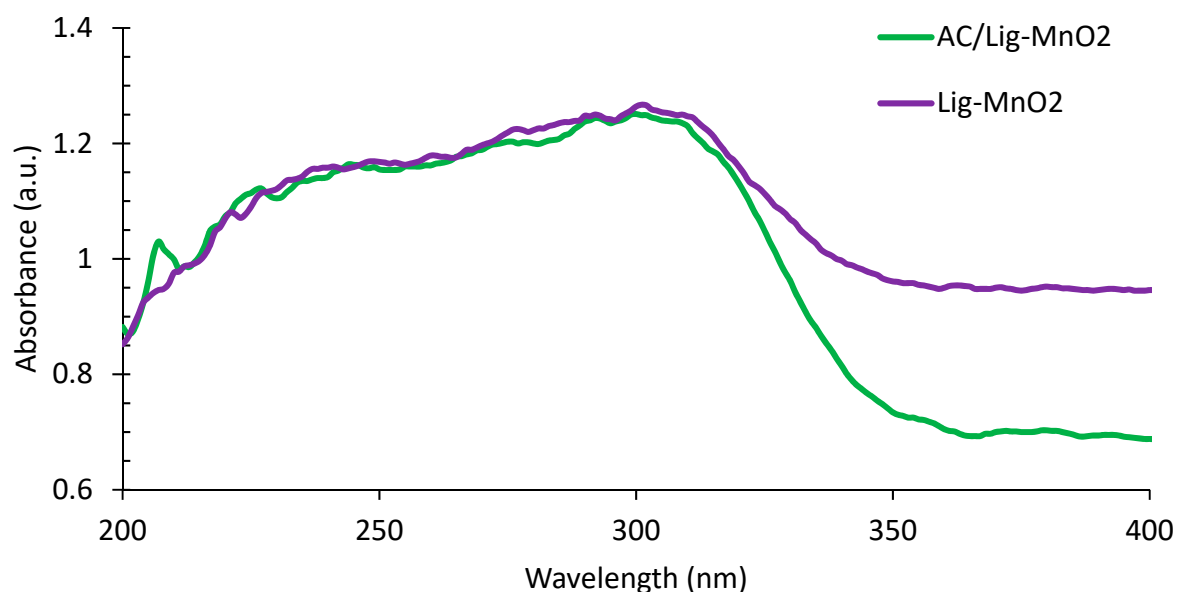


Figure 4. UV-vis spectroscopy of AC/Lig-MnO₂ and Lig-MnO₂.

3.1.4. Powder X-ray Diffraction

The XRD plot in Figure 5a for AC-lignin-MnO₂ shows a broad diffraction peak (002) in the range $2\theta = 15\text{--}30^\circ$, which indicates that the amorphous AC particles dominate in the structure [33]. Lignin-MnO₂ (Figure 5b) showed a broad peak in the range $2\theta = 20\text{--}25^\circ$, indicating its highly amorphous nature. However, another set of peaks is indicative of the MnO₂, which particularly fits the γ -MnO₂ XRD pattern by matching of the main peak between 30° and 35° [34]. The same peak is also observed in the PXRD pattern of AC with a lower intensity. Combining all proof, it is safe to say that both AC-lignin and non-AC-lignin maintain the crystallinity of MnO₂, while the latter does so to a higher degree.

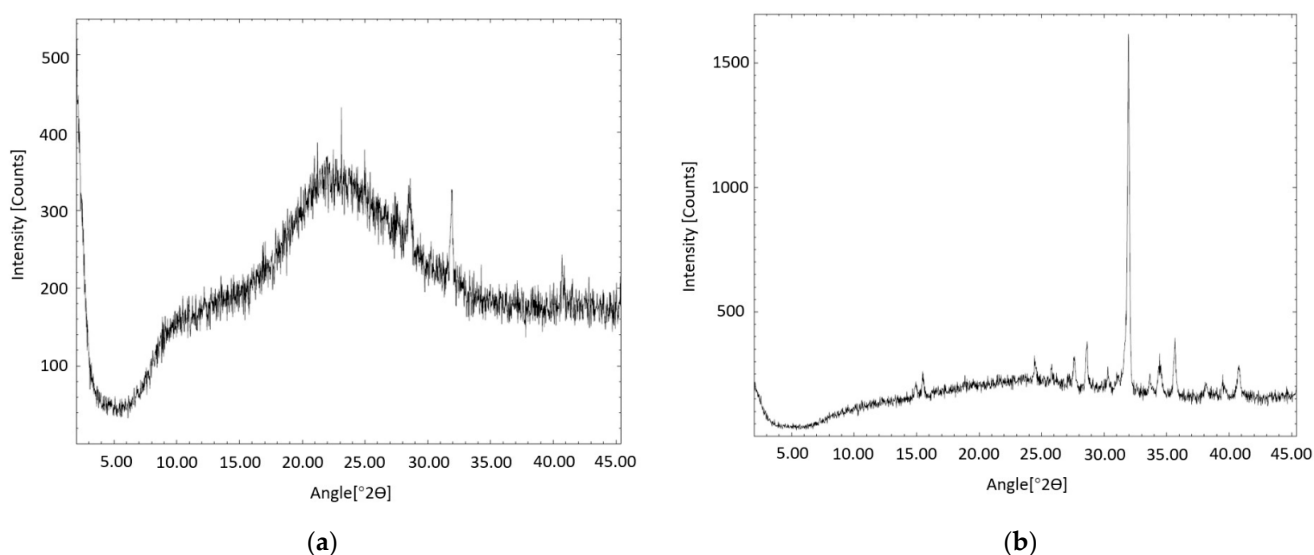
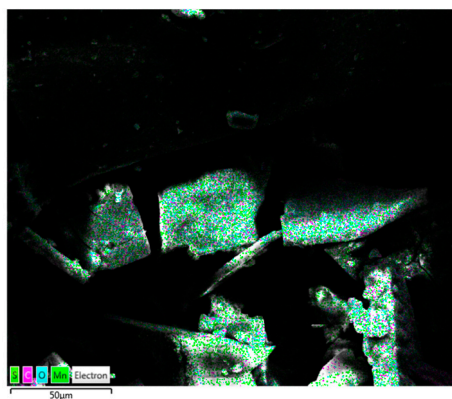
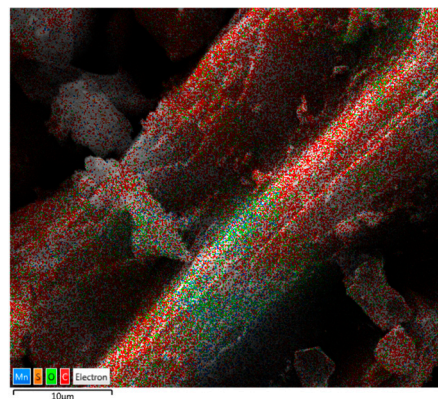
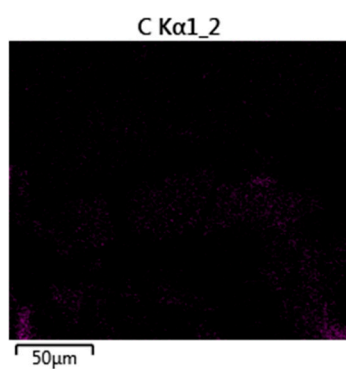


Figure 5. XRD plots of (a) AC/Lig-MnO₂ and (b) Lig-MnO₂.

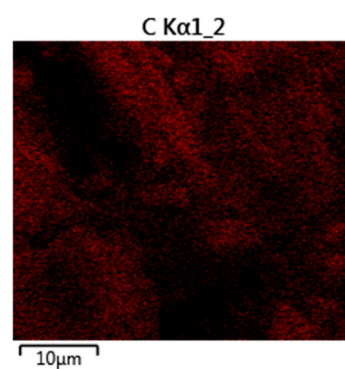
3.1.5. Energy Dispersive X-ray Spectroscopy

EDS mapping (Figure 6) indicates an elemental composition for Sample 1 (Lig/MnO₂) and sample 2 (Ac/Lig/MnO₂) of C/O/Mn/S = 66:27.4:5.5:1.1 (wt.%) and

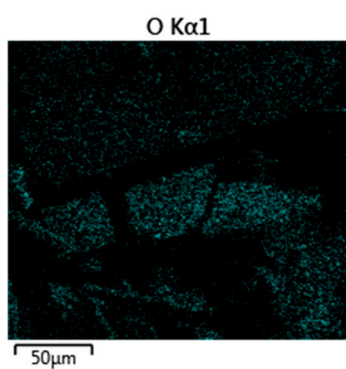
C/O/Mn/S = 36.8:30.7:28.8:3.8 (wt.%), respectively. Element mappings reveal that C, O, Mn, and S atoms are uniformly distributed throughout the entire structure.

(a) Lig-MnO₂(b) AC/Lig/MnO₂

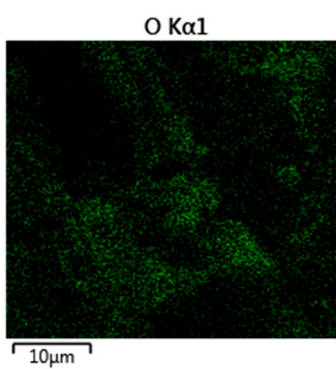
(c)



(d)



(e)



(f)

Figure 6. Cont.

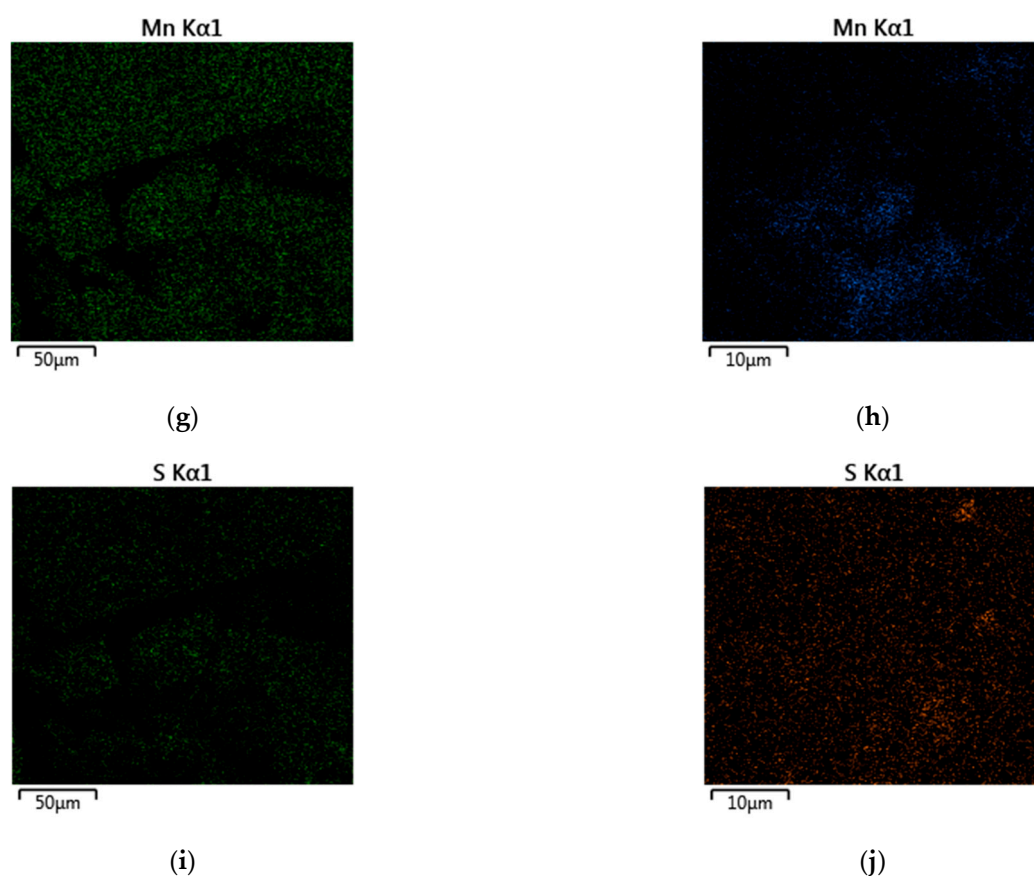


Figure 6. EDS mapping of (a) Lig-MnO₂ and (b) AC/Lig/MnO₂. For Lig-MnO₂, EDS mapping for C (c), O (e), Mn (g), and S (i) are shown. For AC/Lig/MnO₂, EDS mapping for C (d), O (f), Mn (h), and S (j) are also shown.

3.1.6. Electrochemical Analysis

Electrochemical testing is performed to compare and analyze the stability and cycling life of the microwave synthesis-based green composite electrodes. Cyclic voltammetry (CV), cyclic charge-discharge (CCD), and impedance tests were run to explore their potential for supercapacitor applications. CV responses of the AC/Lig-MnO₂ and Lig-MnO₂ samples performed at multiple scan rates are shown in Figure 7a,b. A polymer-gel electrolyte of PVA/H₃PO₄ is used. The operating potential range for both samples is 1.0–2.0 V. The different scan rates implemented are 10, 25, 50, and 100 mV s^{−1}. The rate of diffusion was observed to increase for larger scan rates, and the specific capacitance decreased. This can be attributed to diffusion limitations leading to an ineffective interaction between the electro-active material and the electrolyte. Hence, the scan rate of 10 mV s^{−1} was selected for further CV testing. The CV plots at 10 mV s^{−1} for AC/Lig-MnO₂ and Lig-MnO₂ can be seen in Figure 7c. Figure 7d displays a comparative histogram of the obtained specific capacitance for both materials. The highest specific capacitance obtained for AC/Lig-MnO₂ is 7.4 F g^{−1} (22 mF cm^{−2}), and for Lig-MnO₂ is 1.1 F g^{−1} (12.03 mF cm^{−2}). Initially, during the CV tests, the AC/Lig-MnO₂ supercapacitor displays a higher specific capacitance as compared to Lig-MnO₂. This can be attributed to the higher surface area as well as the high porosity of AC.

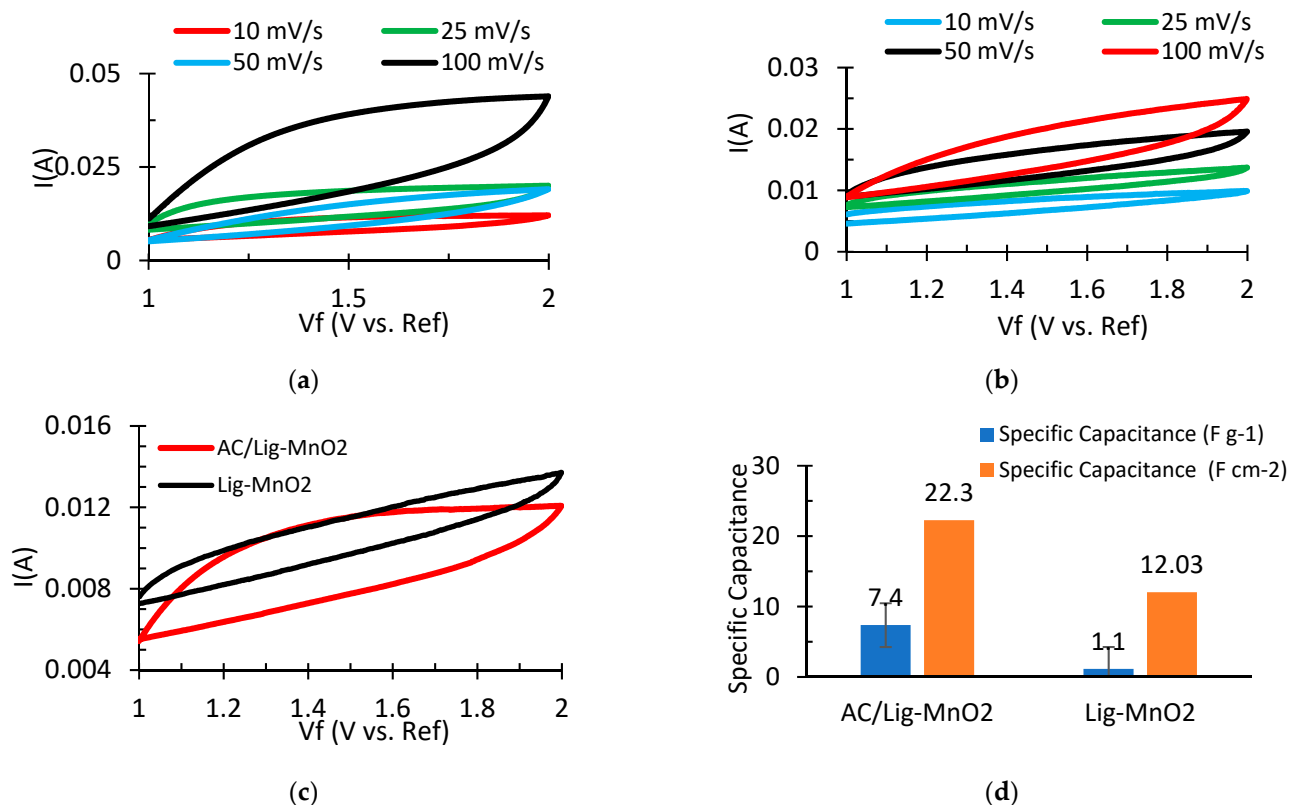


Figure 7. CV plots for (a) AC/Lig-MnO₂, (b) Lig-MnO₂ at various scan rates, (c) comparison of CV plots of AC/Lig-MnO₂ and Lig-MnO₂ at 10 mV s⁻¹, and (d) comparative histogram of specific capacitances.

The cycling life and stability of the system are the most vital requirements for a supercapacitor. To study the pseudo-capacitance behavior further, cyclic charge-discharge (CCD) tests were carried out for 750 cycles at 0.26 A g⁻¹ current density. Figure 8a compares the specific capacitance performance of both materials. The initial specific capacitance for Lig-MnO₂ is 16.22 mF cm⁻², and for AC/Lig-MnO₂ is 14.03 mF cm⁻². After 750 cycles, the final specific capacitance of the Lig-MnO₂ supercapacitor is 16.18 mF cm⁻², and of the AC/Lig-MnO₂ supercapacitor is 12.64 mF cm⁻². Lig-MnO₂ displays a better specific capacitance performance in comparison to AC/Lig-MnO₂. This is due to the presence of a higher number of functional groups in lignin. While AC has a very high surface area and porosity, it does not have as many functional groups present. Therefore, lignin has a comparatively higher pseudo-capacitance than AC. Figure 8b displays the capacitance retention for both supercapacitors. Lig-MnO₂ exhibits a high retention performance of ~99.7%, while AC/Lig-MnO₂ has a retention of ~90%. The lower number of functional groups in AC causes a comparatively quick degradation of the material as compared to lignin. Due to this, AC will degrade quicker than lignin, leading to lower retention. The impact of current density on the discharge voltage and the subsequent variation in specific capacitance can be seen in Figure 8c. As the current density increases from 0.03 to 0.26 mA g⁻¹, the specific capacitance for both supercapacitors decrease. This depicts the general characteristics of a supercapacitor. Figure 8d shows a Ragone plot obtained from the CCD experiment. The Ragone plot depicts the relationship between the energy and power densities at different current densities. The shape of the curve corresponds to those reported in the literature for MnO₂ supercapacitors.

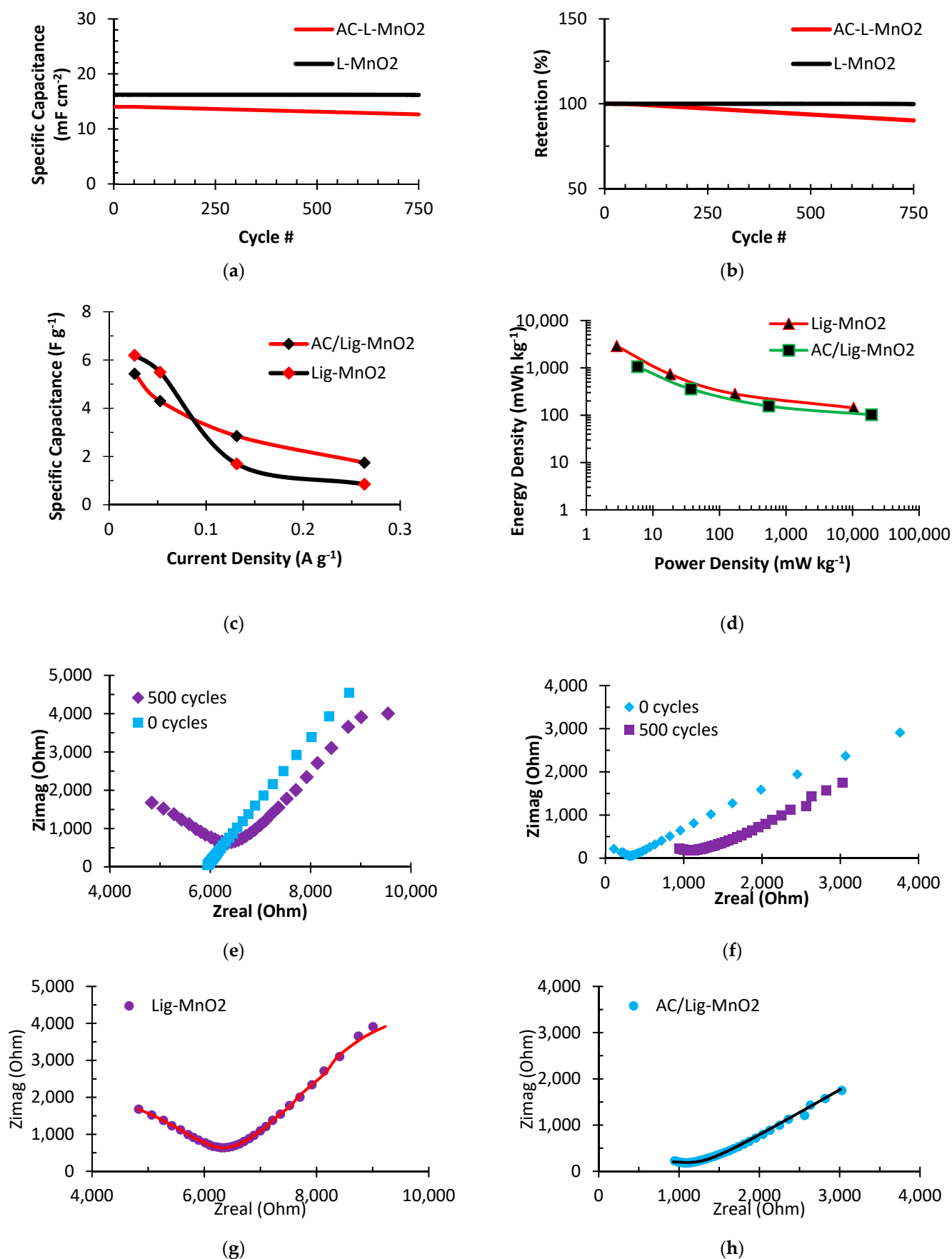
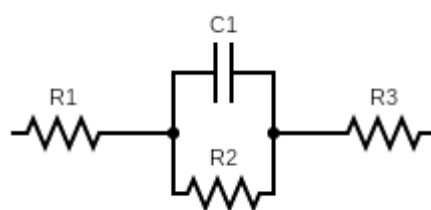


Figure 8. Cont.



(i)

Figure 8. Comparative CCD plots for (a) specific capacitance vs. cycle number, (b) retention (%) vs. cycle number, (c) specific capacitance vs. current density. (d) Ragone plot, (e) EIS plot for Lig-MnO₂ supercapacitor, and (f) EIS plot for AC/Lig-MnO₂ supercapacitor. (g) EIS fitted curve at 500 cycles for Lig-MnO₂ supercapacitor, (h) EIS fitted curve at 500 cycles for AC/Lig-MnO₂ supercapacitor, (i) equivalent circuit for EIS 4.

The electrical double-layer impedance behavior of the supercapacitor was studied via the electrochemical impedance spectroscopy (EIS) test. A frequency range of 0.1–106 Hz, AC Volts = 10 mV, and DC Volts = 1 V was applied. Nyquist plots were obtained at the 0th and the 750th cycle for both supercapacitors, as shown in Figure 8e,f. In Figure 6e, the initial and final impedance were almost the same. For the Lig-MnO₂ supercapacitor, a very small increase in impedance was observed even after 750 cycles. This is in line with the retention performance of the system. The initial impedance was 5945 ohms, and the final impedance was 6493 ohms. The impedance performance of AC/Lig-MnO₂ is shown in Figure 6f. Here, an increase in the impedance can be observed. The initial impedance was 310.8 ohms, and the final impedance was 1089 ohms. As the impedance of the system increases, subsequently, the current flow decreases, leading to lower capacity retention. An equivalent circuit is presented in Figure 6i. The electrolyte resistance (R1), double-layer capacitance (C1), resistance (R2, in parallel with C1), and the electrode diffusion resistance (R3) are shown.

4. Conclusions

In this research, we have successfully synthesized two types of green composite electrodes via microwave synthesis. MnO₂ microparticles were synthesized via microwave irradiation. Due to the high penetration depth and rate of nucleation of microwave irradiation, uniform surface morphology and particle distribution of micro-MnO₂ particles on the lignin and AC/lignin matrices were successfully achieved. The electrochemical evaluation showed the high capacitive performance of lignin-based materials deposited with the microwave-synthesized micro-MnO₂ particles, as compared to that of pure lignin materials. Among the two materials, Lig-MnO₂ exhibited better performance, with a specific capacitance of 16.22 mF cm^{−2} and a ~99.7% capacitance retention. Both materials exhibited capacitance retention of ~90% or higher. In comparison to the reported literature, these materials performed with higher stability and exhibited consistent material structurization with tunable properties. As a result, the high-performing, quasi-solid-state supercapacitors with reduced synthesis time have been successfully fabricated from biomaterials. This work provided a simple and low-cost approach in synthesizing green composite electrodes for supercapacitor applications via microwave irradiation.

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References

- Hall, P.J.; Mirzaeian, M.; Fletcher, S.I.; Sillars, F.B.; Rennie, A.J.R.; Shitta-Bey, G.O.; Wilson, G.; Cruden, A.; Carter, R. Energy storage in electrochemical capacitors: Designing functional materials to improve performance. *Energy Environ. Sci.* **2010**, *3*, 1238–1251. [\[CrossRef\]](#)
- Yan, J.; Wang, Q.; Wei, T.; Fan, Z. Recent Advances in Design and Fabrication of Electrochemical Supercapacitors with High Energy Densities. *Adv. Energy Mater.* **2014**, *4*, 1300816. [\[CrossRef\]](#)
- Inganäs, O.; Admassie, S. 25th Anniversary Article: Organic Photovoltaic Modules and Biopolymer Supercapacitors for Supply of Renewable Electricity: A Perspective from Africa. *Adv. Mater.* **2014**, *26*, 830–848. [\[CrossRef\]](#) [\[PubMed\]](#)
- Liu, Z.; Xu, J.; Chen, D.; Shen, G. Flexible electronics based on inorganic nanowires. *Chem. Soc. Rev.* **2015**, *44*, 161–192. [\[CrossRef\]](#)
- Li, L.; Wu, Z.; Yuan, S.; Zhang, X.-B. Advances and challenges for flexible energy storage and conversion devices and systems. *Energy Environ. Sci.* **2014**, *7*, 2101–2122. [\[CrossRef\]](#)
- Liu, Q.-C.; Xu, J.-J.; Xu, D.; Zhang, X.-B. Flexible lithium–oxygen battery based on a recoverable cathode. *Nat. Commun.* **2015**, *6*, 7892. [\[CrossRef\]](#) [\[PubMed\]](#)
- Chen, Y.; Jha, S.; Raut, A.; Zhang, W.; Liang, H. Performance Characteristics of Lubricants in Electric and Hybrid Vehicles: A Review of Current and Future Needs. *Front. Mech. Eng.* **2020**, *6*, 82. [\[CrossRef\]](#)
- Jha, S.; Chen, Y.; Zhang, B.; Elwany, A.; Parkinson, D.; Liang, H. Influence of morphology on electrochemical and capacity performance of open-porous structured electrodes. *J. Appl. Electrochem.* **2020**, *50*, 231–244. [\[CrossRef\]](#)
- Jha, S.; Ponce, V.; Seminario, J.M. Investigating the effects of vacancies on self-diffusion in silicon clusters using classical molecular dynamics. *J. Mol. Model.* **2018**, *24*, 290. [\[CrossRef\]](#)
- Renner, P.; Jha, S.; Chen, Y.; Raut, A.; Mehta, S.G.; Liang, H. A Review on Corrosion and Wear of Additively Manufactured Alloys. *J. Tribol.* **2021**, *143*, 050802. [\[CrossRef\]](#)
- Yang, Z.; Tian, J.; Yin, Z.; Cui, C.; Qian, W.; Wei, F. Carbon nanotube- and graphene-based nanomaterials and applications in high-voltage supercapacitor: A review. *Carbon* **2019**, *141*, 467–480. [\[CrossRef\]](#)
- Jha, S.; Mehta, S.; Chen, E.; Sankar, S.S.; Kundu, S.; Liang, H. Bimetallic tungstate nanoparticle-decorated-lignin electrodes for flexible supercapacitors. *Mater. Adv.* **2020**, *1*, 2124–2135. [\[CrossRef\]](#)
- Jha, S.; Mehta, S.; Chen, Y.; Renner, P.; Sankar, S.S.; Parkinson, D.; Kundu, S.; Liang, H. NiWO₄ nanoparticle decorated lignin as electrodes for asymmetric flexible supercapacitors. *J. Mater. Chem. C* **2020**, *8*, 3418–3430. [\[CrossRef\]](#)
- Mehta, S.; Jha, S.; Liang, H. Lignocellulose materials for supercapacitor and battery electrodes: A review. *Renew. Sustain. Energy Rev.* **2020**, *134*, 110345. [\[CrossRef\]](#)
- Archuleta, M.M. Toxicity of materials used in the manufacture of lithium batteries. *J. Power Sources* **1995**, *54*, 138–142. [\[CrossRef\]](#)
- Inagaki, M.; Konno, H.; Tanaike, O. Carbon materials for electrochemical capacitors. *J. Power Sources* **2010**, *195*, 7880–7903. [\[CrossRef\]](#)
- Zhang, W.; Yin, J.; Lin, Z.; Lin, H.; Lu, H.; Wang, Y.; Huang, W. Facile preparation of 3D hierarchical porous carbon from lignin for the anode material in lithium ion battery with high rate performance. *Electrochim. Acta* **2015**, *176*, 1136–1142. [\[CrossRef\]](#)
- Zhang, X.; Glösen, A.; Garcia-Valls, R. Porous lignosulfonate membranes for direct methanol fuel cells. *J. Membr. Sci.* **2006**, *276*, 301–307. [\[CrossRef\]](#)
- Juikar, S.J.; Vigneshwaran, N. Extraction of nanolignin from coconut fibers by controlled microbial hydrolysis. *Ind. Crop. Prod.* **2017**, *109*, 420–425. [\[CrossRef\]](#)
- Ma, W.; Chen, S.; Yang, S.; Chen, W.; Weng, W.; Cheng, Y.; Zhu, M. Flexible all-solid-state asymmetric supercapacitor based on transition metal oxide nanorods/reduced graphene oxide hybrid fibers with high energy density. *Carbon* **2017**, *113*, 151–158. [\[CrossRef\]](#)
- Jha, S.; Mehta, S.; Chen, Y.; Likhari, R.; Stewart, W.; Parkinson, D.; Liang, H. Design and synthesis of high performance flexible and green supercapacitors made of manganese-dioxide-decorated alkali lignin. *Energy Storage* **2020**, *2*, e184. [\[CrossRef\]](#)
- Jha, S.; Mehta, S.; Chen, Y.; Ma, L.; Renner, P.; Parkinson, D.Y.; Liang, H. Design and Synthesis of Lignin-Based Flexible Supercapacitors. *ACS Sustain. Chem. Eng.* **2020**, *8*, 498–511. [\[CrossRef\]](#)
- Zhang, Q.-Z.; Zhang, D.; Miao, Z.-C.; Zhang, X.-L.; Chou, S.-L. Research Progress in MnO₂–Carbon Based Supercapacitor Electrode Materials. *Small* **2018**, *14*, 1702883. [\[CrossRef\]](#) [\[PubMed\]](#)
- Meher, S.K.; Rao, G.R. Enhanced activity of microwave synthesized hierarchical MnO₂ for high performance supercapacitor applications. *J. Power Sources* **2012**, *215*, 317–328. [\[CrossRef\]](#)
- Wang, P.; Zhao, Y.-J.; Wen, L.-X.; Chen, J.-F.; Lei, Z.-G. Ultrasound–Microwave-Assisted Synthesis of MnO₂ Supercapacitor Electrode Materials. *Ind. Eng. Chem. Res.* **2014**, *53*, 20116–20123. [\[CrossRef\]](#)
- Liu, D.; Wang, Y.; Jia, B.; Wei, J.; Liu, C.; Zhu, J.; Tang, S.; Wu, Z.; Chen, G. Microwave-Assisted Hydrothermal Preparation of Corn Straw Hydrochar as Supercapacitor Electrode Materials. *ACS Omega* **2020**, *5*, 26084–26093. [\[CrossRef\]](#)

-
27. Seong, K.-d.; Jin, X.; Kim, D.; Kim, J.M.; Ko, D.; Cho, Y.; Hwang, M.; Kim, J.-H.; Piao, Y. Ultrafast and scalable microwave-assisted synthesis of activated hierarchical porous carbon for high-performance supercapacitor electrodes. *J. Electroanal. Chem.* **2020**, *874*, 114464. [CrossRef]
 28. Mylarappa, M.; Lakshmi, V.; Mahesh K R, V.; H P, N.; Raghavendra, N. A facile hydrothermal recovery of nano sealed MnO₂ particle from waste batteries: An advanced material for electrochemical and environmental applications. *IOP Conf. Ser. Mater. Sci. Eng.* **2016**, *149*, 012178. [CrossRef]
 29. Mayerhöfer, T. Wave Optics in Infrared Spectroscopy. 2021. Available online: <https://www.researchgate.net/project/Book-Project-Wave-Optics-in-Infrared-Spectroscopy> (accessed on 12 August 2021).
 30. Azimvand, J.; Didehban, K.; Mirshokrai, S.A. Preparation and characterization of lignin polymeric nanoparticles using the green solvent Ethylene glycol: Acid precipitation technology. *BioResources* **2018**, *13*, 2887–2897. [CrossRef]
 31. Nandiyanto, A.B.D.; Oktiani, R.; Ragadhita, R. How to read and interpret FTIR spectroscopy of organic material. *Indones. J. Sci. Technol.* **2019**, *4*, 97–118. [CrossRef]
 32. Zhang, S.; Wang, Z.; Zhang, Y.; Pan, H.; Tao, L. Adsorption of methylene blue on organosolv lignin from rice straw. *Procedia Environ. Sci.* **2016**, *31*, 3–11. [CrossRef]
 33. Liu, X.-Y.; Huang, M.; Ma, H.-L.; Zhang, Z.-Q.; Gao, J.-M.; Zhu, Y.-L.; Han, X.-J.; Guo, X.-Y. Preparation of a carbon-based solid acid catalyst by sulfonating activated carbon in a chemical reduction process. *Molecules* **2010**, *15*, 7188–7196. [CrossRef] [PubMed]
 34. Musil, M.; Choi, B.; Tsutsumi, A. Morphology and Electrochemical Properties of α -, β -, γ -, and δ -MnO₂ Synthesized by Redox Method. *J. Electrochem. Soc.* **2015**, *162*, A2058–A2065. [CrossRef]