Schriftenreihe des Fachgebiets
Konversionstechnologien nachwachsender Rohstoffe

Hrsg. Prof. Dr. Andrea Kruse

DISSERTATION

Development of Carbon Materials for Microbial Fuel Cells

Musa Bishir

Band 9

Konversions Technologien

UNIVERSITÄT HOHENHEIM

Development of Carbon Materials for Microbial Fuel Cells

Dissertation to obtain the doctoral degree of Agricultural Sciences (Dr. sc. agr.)

Faculty of Agricultural Sciences
University of Hohenheim

Institute of Agricultural Engineering

submitted by

Musa BISHIR

Bakori, Nigeria

2022

This thesis was accepted as a doctoral thesis (Dissertation) in fulfilment of the regulations to acquire the doctoral degree “Doktor der Agrarwissenschaften” (Dr. sc. agr. / Ph.D. in Agricultural Sciences) by the Faculty of Agricultural Sciences at University of Hohenheim on 27th July 2022.

Date of the oral examination: 5th September 2022

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Development of Carbon Materials for Microbial Fuel Cells

D 100 (Diss. Universität Hohenheim)

Shaker Verlag
Düren 2022

Bibliographic information published by the Deutsche Nationalbibliothek
The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available in the Internet at http://dnb.d-nb.de.

Zugl.: Hohenheim, Univ., Diss., 2022

Printed in Germany.

ISBN 978-3-8440-8815-1
ISSN 2512-0042

Shaker Verlag GmbH • Am Langen Graben 15a • 52353 Düren
Phone: 0049/2421/99011-0 • Telefax: 0049/2421/99011-9
Internet: www.shaker.de • e-mail: info@shaker.de

Printed and/or published with the support of the German Academic Exchange Service

Special thanks to Nigerian Petroleum Technology Development Fund (PTDF) and Deutscher Akademischer Austausch-Dienst (DAAD) for the sponsorship during the study period.

This Dissertation is dedicated to my mother, Malama Zainab Musa and my late father, Malam Bashir Mohamed Bakori. May God Almighty have mercy on him, Aameen. Also, to my Wife (Malama Hafiza Lukman), Children (Zainab & Aisha) and all my Siblings.

DECLARATION

Affidavit

pursuant to Sec. 8(2) of the University of Hohenheim's doctoral degree regulations for Dr. sc. agr.

1. I hereby declare that I independently completed the doctoral thesis submitted on the topic

Development of Carbon Materials for Microbial Fuel Cells

……..……

2. I only used the sources and aids documented and only made use of permissible assistance by third parties. In particular, I properly documented any contents which I used - either by directly quoting or paraphrasing - from other works.

3. I did not accept any assistance from a commercial doctoral agency or consulting firm.

4. I am aware of the meaning of this affidavit and the criminal penalties of an incorrect or incomplete affidavit.

I hereby confirm the correctness of the above declaration. I hereby affirm in lieu of oath that I have, to the best of my knowledge, declared nothing but the truth and have not omitted any information.

Tübingen, 11.09.2022

…… ……..

(Place, date) (Signature)

ACKNOWLEDGEMENTS

It is a great honour for me to express my profound and cordial gratitude to my research supervisor, Prof. Dr. Andrea Kruse for her guidance, skilled advice, and support during the period of my study. Special thanks also to co-reviewers of my doctoral dissertation; Prof. Dr. Nicolaus Dahmen and Prof. Dr. Joachim Müller for their supports and contributions.

I would like to appreciate the Nigerian Government, especially the management of the Nigerian Petroleum Technology Development Fund (PTDF) and also the German Academic Exchange Service (DAAD), for the sponsorship I received throughout my program. Also, to my employer, the management of Ahmadu Bello University, Zaria Nigeria, for the study fellowship (Study Leave) awarded to me, to enable me to pursue my doctorate at the University of Hohenheim, Stuttgart, Germany.

A part of this work was carried out in collaboration with Ms. Maryam Tariq [1], who was a Master Student at the Department of Conversion Technologies of Biobased Resources, Institute of Agricultural Engineering, University of Hohenheim. Her contributions have been duly acknowledged as a co-author of some of the papers included in this dissertation. I am also indebted to recognise the support and contributions I received from Mrs. Veronika Ege, Dr. Catalina Rodriguez-Correa and all my doctoral and postdoctoral colleagues, especially Dr. Pablo Arauzo, Dr. Muhammad-Jamal Alhnidi, Mr. Dominik Wüst, Mr. Joshua Ajikashile, Dr. Jan Straten as well as Mr. Maciej Olszewski. Special thanks also to the staff of the Institute's workshop, particularly Mr. Bersi Gianluca, Mr. Ralph Drescher, Mr. Alexander Smolin among others, who assisted in various capacities, ranging from construction of MFC reactors to circuit preparation and so on during the study.

I would like to also thank Prof. Dr. Julia Fritz-Steuber, Ms. Lena Schleicher, and Mrs. Luise Weber of Institute of Biology, University of Hohenheim, as well as Prof. Dr. Kai Thormann of Justus Liebig University Giessen, for providing me with the *Shewanella oneidensis* MR-1 strain used in this study, and for other technical assistance.

I am very grateful to my family, especially my parents, wife, children, and siblings (Abdullahi, Aisha, Bello, Usman, Inuwa etc.), and to my friends who always encouraged and supported me. Finally, my sincere appreciation to any other person not mentioned here, who provided his/her support in one way or the other to make this work a success.

LIST OF UNITS, SYMBOLS & ABBREVIATIONS

Symbols & Abbreviations

MFC Microbial Fuel Cell
HTC Hydrothermal Carbonization
HPLC High-Performance Liquid Chromatography
KOH Potassium Hydroxide
BET Brunauer-Emmett-Teller
COD Chemical Oxygen Demand
NAC Non-activated Corncob Pyrochar
SAC Steam-activated Corncob Pyrochar
KAC KOH-activated Corncob Pyrochar
SA_{BET} Specific BET Surface Area
PD Pore Diameter / Å
PV Pore Volume
ϱ Bulk density / kg m^{-3}.
σ Electrical Conductivity / S
ε^c Coulombic efficiency / %
p Pressure / Pa.
F_g Weight load / N.
m_w Mass of added weight / Kg.
g Earth's acceleration (9.81 ms^{-2})
A Piston ground area / m^2
h Height of the pyrochar sample in glass cylinder / m.
R Ohmic resistance / Ω.
m Mass of the sample in kg.
V Volume of the sample in the cylinder / m^3
CR Compression ratio
$Vp1$ Volume at applied pressure 1 (blank weight) / m^3
$Vp4$ Volume at applied pressure 4 (weight 10 kg) / m^3
Ag/AgCl silver/silver chloride

Units

Ω	Ohm
Å	Ångström
L	Litre
S	Siemens
µ	Micro
W	Watt
A	Ampere
V	Volt
Pa	Pascal
N	Newton
Kg	Kilogramm
m	meter
s	second
%	Percent

SUMMARY

Doctoral Candidate: Musa BISHIR

Doctoral Thesis Title: Development of Carbon Materials for Microbial Fuel Cells

There are growing interests in microbial fuel cells (MFCs) for anaerobic bioenergy generation. MFC uses electrodes and organic wastewater as substrate for electrogenic bacteria, to catabolize and generate power. Researchers in this discipline continue to be most interested in finding suitably affordable electrode materials. However, despite the large varieties of commercially available electrodes, only few are suitable for electro-active bacterial colonization, during biofilm formation in microbial fuel cells (MFCs), and most of these electrodes are cost prohibitive. Hence there is need to search for low-cost alternative electrodes for MFCs. The focus of this study was to develop electrodes locally from corncob biomass for application in microbial fuel cells. Pyrochars were produced by pyrolysis (600 °C and a continuous flow rate of 3 NL/min of nitrogen gas for 30 min) and subsequently steam or potassium hydroxide (KOH) activation of the pyrochar at 600 °C were carried out accordingly. Physicochemical, structural, and electrochemical properties of the activated and non-activated pyrochars were determined according to standardized analytical methods. A comparative bioelectricity generation from process water of hydrothermal carbonization (HTC) of spent bear grains (pH = 5.99) and treated–biogas digestate (pH = 7.97), was carried out in dual-chambered MFCs, using graphite rod (non-porous and very low surface area) and the locally developed potassium hydroxide (KOH)–activated corncob pyrochar (KAC) and steam- activated corncob pyrochar (SAC) electrodes. In all the MFC systems of this study, a standard strain of actively dividing cells of the electroactive bacterium *Shewanella*

oneidensis MR-1, which were at logarithmic phase of growth (24 h) was used as inoculum for bioelectricity generation. According to BET measurements, 1626 $m^2 g^{-1}$ surface area and 14.74 Å pore diameter were obtained from the KOH-activated pyrochar, which was also the most conductive (0.26 S m^{-1}) carbon material used here. The highest power outputs achieved were 323.8 µW and 316.8 µW from HTC process water with SAC and biogas digestate with KAC electrodes, respectively, at an external load of 47 Ω. The initial Chemical Oxygen Demand (48780 mg / L), Dissolved Organic Carbon (4000 mg / L), and Total bounded Nitrogen (5600 mg / L) of the biogas digestate decreased significantly to 36405, 3610 and 4300 mg / L, respectively, in the MFC with KAC electrodes. A Coulombic efficiency of 75 % was recorded from the MFC operated with treated biogas digestate and KAC electrode in a significantly shorter residence time, making it more efficient than its counterpart with SAC electrode, which had a lower Coulombic efficiency of 64 %. In conclusion, chemical activation of pyrochar with KOH resulted in increased electrical conductivity (EC), pore diameter, and most importantly the material's surface area according to the findings. Therefore, KOH-activated corncob pyrochar holds potentials for producing electrode materials with desirable characteristics for successful application in MFC compared to the non-activated and steam-activated pyrochars of the same biomass.

ZUSAMMENFASSUNG

Doctoral Candidate: Musa BISHIR

Doctoral Thesis Title: Entwicklung von Kohlenstoffmaterialien für mikrobielle Brennstoffzellen

Das Interesse an mikrobiellen Brennstoffzellen (MFC) zur anaeroben Bioenergieerzeugung wächst. MFC verwenden Elektroden und organische Abwässer als Substrat für elektrogene Bakterien, die diese abbauen und Strom erzeugen. Das größte Interesse der Forscher in diesem Bereich gilt nach wie vor der Suche nach geeigneten und erschwinglichen Elektrodenmaterialien. Trotz der großen Auswahl an kommerziell erhältlichen Elektroden sind jedoch nur wenige für die Besiedlung mit elektroaktiven Bakterien während der Biofilmbildung in mikrobiellen Brennstoffzellen (MFC) geeignet, und die meisten dieser Elektroden sind unerschwinglich. Daher besteht die Notwendigkeit, nach kostengünstigen alternativen Elektroden für MFCs zu suchen. Der Schwerpunkt dieser Studie lag auf der Entwicklung von Elektroden aus Maiskolben-Biomasse für den Einsatz in mikrobiellen Brennstoffzellen. Pyrochars wurden durch Pyrolyse (600 °C und eine kontinuierliche Durchflussrate von 3 NL/min Stickstoffgas für 30 Minuten) hergestellt und anschließend mit Dampf oder Kaliumhydroxid (KOH) bei 600 °C aktiviert. Die physikalisch-chemischen, strukturellen und elektrochemischen Eigenschaften der aktivierten und nicht aktivierten Pyrochars wurden nach standardisierten analytischen Methoden bestimmt. Eine vergleichende Bioelektrizitätserzeugung aus Prozesswasser der hydrothermalen Karbonisierung (HTC) von Biertrebern (pH = 5,99) und behandeltem Biogasgärrest (pH = 7,97) wurde in Zweikammer-MFCs unter Verwendung von Graphitstäben (nicht porös und

mit sehr geringer Oberfläche) und den vor Ort entwickelten Kaliumhydroxid (KOH)-aktivierten Maiskolbenpyrochars (KAC) und dampfaktivierten Maiskolbenpyrochars (SAC) durchgeführt. In allen MFC-Systemen dieser Studie wurde ein Standardstamm von sich aktiv teilenden Zellen des elektroaktiven Bakteriums *Shewanella oneidensis* MR-1, die sich in der logarithmischen Wachstumsphase (24 h) befanden, als Inokulum für die Erzeugung von Bioelektrizität verwendet. Nach BET-Messungen ergab sich eine Oberfläche von 1626 $m^2 g^{-1}$ und ein Porendurchmesser von 14,74 Å für den KOH-aktivierten Pyrochar, der auch das leitfähigste (0,26 S m^{-1}) der hier verwendeten Kohlenstoffmaterialien war. Die höchsten Leistungen wurden mit 323,8 µW und 316,8 µW aus HTC-Prozesswasser mit SAC- bzw. Biogas-Gärgut mit KAC-Elektroden bei einer externen Belastung von 47 Ω erzielt. Der anfängliche chemische Sauerstoffbedarf (48780 mg / L), der gelöste organische Kohlenstoff (4000 mg / L) und der gesamte gebundene Stickstoff (5600 mg / L) des Biogasgärrestes sanken in der MFC mit KAC-Elektroden deutlich auf 36405, 3610 bzw. 4300 mg / L. Die mit behandeltem Biogasgärrest und KAC-Elektrode betriebene MFC erreichte einen Coulomb-Wirkungsgrad von 75 % bei deutlich kürzerer Verweilzeit und war damit effizienter als ihr Gegenstück mit SAC-Elektrode, das einen niedrigeren Coulomb-Wirkungsgrad von 64 % aufwies. Zusammenfassend lässt sich sagen, dass die chemische Aktivierung von Pyrochar mit KOH zu einer Erhöhung der elektrischen Leitfähigkeit (EC), des Porendurchmessers und vor allem der Oberfläche des Materials führte. Daher hat KOH-aktivierte Maiskolben-Pyrokohle das Potenzial, Elektrodenmaterialien mit wünschenswerten Eigenschaften für eine erfolgreiche Anwendung in MFC herzustellen, verglichen mit nicht-aktivierten und dampf-aktivierten Pyrochars der gleichen Biomasse.

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