UNIVERSITI MALAYSIA PERLIS

International Journal of Nanoelectronics and Materials

IJNeaM

ISSN 198-5761 | E-ISSN 2232-1535

Banana Stem Waste as a Sustainable Modifier for Microstructure Modification of Protonic Ceramic Fuel Cell Cathode

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ABSTRACT

This study investigates the feasibility of utilizing banana stem waste (BSW) as a pore former to modify the microstructure of the PCFC composite cathode. The microstructure of the $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\alpha}$-$Ba(Ce_{0.6}Zr_{0.4})_{0.9}Y_{0.1}O_{3-\delta}$ (LSCF-BCZY64) composite cathode was modified by varying the amounts of the incorporated banana stem waste. The samples underwent sintering at 1000 ˚C, and their microstructural and physical properties were analyzed using X-ray diffraction, scanning electron microscopy, and densimeter. The results indicate that the incorporation of BSW enhances the porosity of the cathode without significantly affecting its crystalline structure. As the amount of BSW increased from 10 to 40 wt.%, the porosity level increased from 7.0% to 32.7%, and the density of the samples decreased from 1.3 to 0.9 g/cm3, thereby supporting the results of the porosity analysis. Increased cathode porosity can enhance reactant accessibility to active sites, potentially resulting in improved cell performance and durability. Moreover, the utilization of BSW as a sustainable and cost-effective pore former aligns with the growing emphasis on environmentally friendly materials in energy applications.

Keywords: *Protonic ceramic fuel cell, composite cathode, microstructure, pore-former*

1. INTRODUCTION

Protonic ceramic fuel cell (PCFC) is a highly efficient and sustainable energy generation system. It utilizes a proton-conducting ceramic electrolyte in contrast to the conventional oxygen-ion conducting solid oxide fuel cell (SOFC). Compared to SOFC, PCFC applications offer higher efficiency and faster startup times. Like SOFC, PCFC comprises three main parts: anode, electrolyte, and cathode.

The cathode is a critical component of PCFC as it is responsible for the reduction of oxygen to produce water and generate electricity. It has a significant impact on cell performance since the electrochemical activity and efficiency of the cathode govern the performance of the entire PCFC. To increase the effectiveness and durability of PCFC, tremendous research has been devoted to enhancing cathode performance. This entails creating novel cathode materials with improved electrochemical activity, tailoring the cathode's microstructure to increase its transport capabilities, and optimizing the cathode composition to maximize the cell's overall performance [1-3].

Optimizing the microstructure of the cathode, particularly its porosity, is crucial to maximizing the performance and efficiency of PCFC. An ideal microstructure provides good contact between the cathode and electrolyte phases thus enlarging the triple-phase-boundary, which is the active site for the electrochemical reactions [3]. The cathode's porosity affects the cathode's transport properties and determines the accessibility of the active sites to oxygen. A higher porosity facilitates better oxygen diffusion to the active sites, which can improve the performance of the cathode and eventually enhance the performance of the whole cell. Therefore, it is crucial to carefully design and control the cathode microstructure to achieve high performance and efficiency in PCFC.

Toward this end, various approaches have been suggested to impart suitable porosity to the electrode membrane for enhanced gas diffusion or electrical conductivity [4, 5]. Among these methods, the most widely accepted and effective technique for creating a porous microstructure involves the incorporation of pore formers into the initial powders of the electrode material. Commonly employed pore formers include starch, carbon black, graphite, and spherical polymers [6-8]. Lifang et.al [6] studied the effect of different pore formers on the microstructure and performance of cathode membranes for the solid oxide fuel cell. They found that the shape of the pores, the pore size, and the pore distribution in the final ceramic are related to the type of pore formers utilized. The properties of a porous electrode material are not solely determined by its overall porosity but also by the distribution of pore sizes within the material. Hu et al. [9] observed that increasing the loading of pore formers in the electrode materials results in higher porosity, including an increased number of larger pores. This heightened pore-former loading can lead to the generation of electrode materials with elevated levels of high- and open-porosity.

While significant progress has been made in this area, there remains a need for sustainable and cost-effective pore formers that can address the limitations of current materials. The use of biowaste as pore formers in PCFC cathodes presents a promising avenue to achieve these goals. Biowaste, such as banana stem waste, offers several advantages, including abundant availability, low cost, and environmental sustainability [10]. Previous studies have explored the use of various pore formers in PCFC cathodes, including carbon-based materials and polymers [6-8]. However, these materials often suffer from limitations such as high cost, limited availability, and environmental concerns. In contrast, banana stem waste is a renewable resource that is often discarded as waste, making it an attractive option for sustainable pore former materials.

The selection of banana stem waste as a pore former is reinforced by its characteristics, including its high cellulose content, low ash content, and favorable thermal stability [11]. These attributes indicate that banana stem waste has the potential to effectively alter the microstructure of PCFC cathodes, thereby improving their performance. This study specifically addresses the gap in knowledge concerning the utilization of banana stem waste as a pore former in LSCF-BCZY composite cathodes for PCFCs. Banana stems represent a plentiful and environmentally friendly resource for tailoring cathode microstructures. Through the incorporation of banana stem waste, we aim to augment the cathode's surface area and porosity, potentially leading to enhanced PCFC performance. This initial investigation focuses on two primary objectives: establishing the feasibility of banana stem waste as a pore former and determining the optimal amount to maximize its beneficial effects on cathode morphology. Ultimately, this research not only lays the groundwork for future optimization of this sustainable approach but also sets the stage for exploring synergistic effects with other cathode modifications.

2. METHODOLOGY

The La0.6Sr0.4Co0.2Fe0.8O3-α (LSCF) and Ba(Ce0.6Zr0.4)0.9Y0.1O3-δ (BCZY) ceramic powders were prepared by the method described in our previous work [12]. Fabrication of the composite cathode was performed by mixing pure phases of both powders in a 1:1 weight ratio. Banana stem waste (BSW) was sourced from a farm in Jeniang, Kedah, Malaysia. The banana stem was cut into small pieces and dried in the oven at 80°C for 24 h to eliminate moisture. The dried stems were then ground into powders and sieved through a 63 µm sieve to ensure uniform particle size. Various amounts of BSW (10-40 wt.%) were incorporated into the composite cathode powder to investigate their impact on pore formation, denoted as BS10, BS20, BS30, and BS40, representing the addition of 10 to 40 wt.% of BSW.

The powder mixtures were homogenized in an agate mortar and compacted at 5 tons to form a sample disk approximately 15 mm in diameter. Samples were then thermally treated in a furnace at 1000°C for 5 h to remove the pore former. The experimental design included triplicate samples for each condition, with the unmodified composite cathode of LSCF-BCZY serving as the control sample.

Characterization of the samples involved X-ray diffraction (XRD), scanning electron microscopy (SEM), and density analysis. Porosity was estimated using image analysis software (Image J 1.45p) employing the threshold technique.

3. RESULT & DISCUSSION

3.1. Characterization of Banana Stem Waste as the Pore Former

Figure 1 displays the FTIR spectrum obtained from powdered banana stem waste. Notably, the analysis revealed prominent peaks at 3235.51 cm-1, unequivocally confirming the presence of alkyne groups distinguished by C-H stretching in lignin, hemicellulose, and cellulose. This outcome concurs with previous findings reported by Noremberg et al. [13], which similarly identified cellulose spectra in banana stems. Furthermore, characteristic signals commonly associated with cellulose were evident, encompassing the stretching of the C-O ring within the range of 1052–1032 cm-1, as well as the vibrational stretching modes of –OH, C–H, and C–O–C pyranose rings at 1161 cm-1 [14].

Additionally, a striking peak at 1686.43 cm-1 was detected, signifying the presence of conjugated ketone groups with C=O stretching frequencies. These groups are typically associated with carbohydrates, aromatic ethers, esters, and polysaccharides and are likely attributed to the presence of Fe and other salts in banana stems. This finding aligns with the research conducted by Khatua et al. [15], which identified aromatic groups, aromatic ethers, and polysaccharides in banana stems.

Furthermore, the presence of a peak at 1264.58 cm-1 strongly implies the existence of aromatic esters characterized by C-O stretching. Finally, a conspicuous peak at 1380 cm-1, indicative of the stretching of N-O bonds typically found in nitrate compounds, provides compelling evidence for the presence of nitrogen in the banana stem [15]. The distinctive peaks and patterns observed in the FTIR spectrum, in conjunction with existing literature validating the presence of cellulose and other relevant spectra in banana stems, underscore the suitability of this agricultural byproduct for enhancing porosity in composite cathodes.

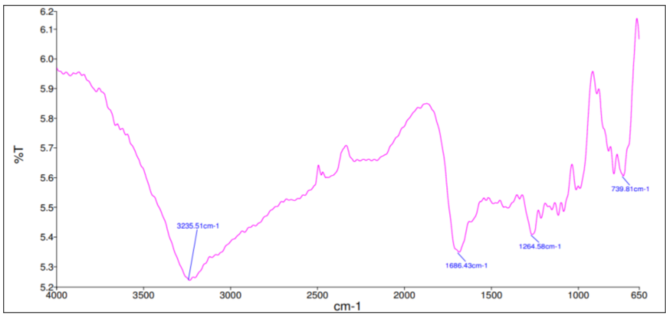

Figure 1. FTIR spectrum of the banana stem waste powder.

Figure 2 provides an intricate examination of the morphology of banana stem waste powder at a magnification of x 2000. This detailed micrograph unveils the complex structure of the banana stem's constituent fibers, which are primarily composed of cellulose. These cellulose fibers play a pivotal role in the structural integrity of the banana stem. They exhibit a striking elongated and slender configuration, with an average diameter between 5-6 μm. This characteristic feature underscores the importance of cellulose in providing the plant with mechanical strength and support.

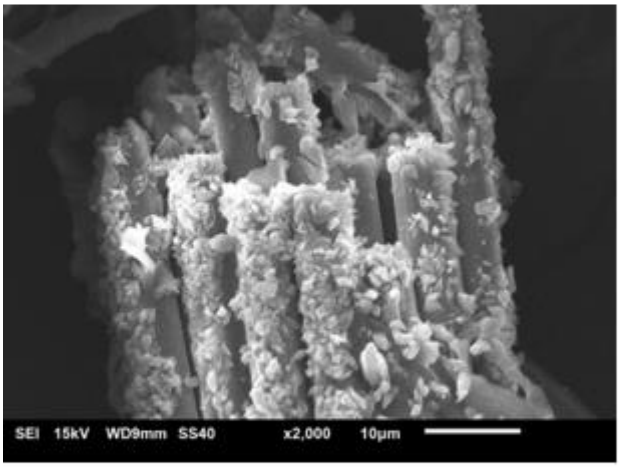

Figure 2. SEM micrograph of the banana stem waste powder.

The micrograph reveals a surface texture of these fibers that displays some non-uniformity. This variability is primarily linked to the existence of non-cellulosic constituents, notably lignin and pectin [16]. These constituents play a significant role in determining the overall texture of the fibers, introducing a level of surface roughness and irregularity. These findings provide valuable insight into the intricate microstructure of banana stem waste, emphasizing the prevalence of cellulose fibers while also acknowledging the presence of non-cellulosic elements. These unique fiber properties hold substantial promise for diverse potential applications. Understanding the pore former's microstructure is fundamental, allowing us to predict the potential changes it might induce in the final material.

The analysis of thermal decomposition plays a crucial role in refining the firing conditions during the production of the composite cathodes. In a comprehensive study by Abdullah et al. [17] and Cheng et al. [18] on the thermal decomposition of banana stem, primary pyrolysis reactions, including depolymerization, decarboxylation, and cracking, were observed within the temperature range of 150°C to 660°C. Specifically, the thermal degradation of hemicellulose and cellulose occurs at approximately 322°C. The insight into the thermal decomposition of the pore-forming material ensures the thorough combustion of the pore-forming material, leaving no residue, a critical requirement for achieving the targeted porosity in the composite cathode structure.

3.2. Reactivity Study of the Composite Cathode Upon the Addition of Pore Former

The chemical compatibility between banana stem waste (BSW) and the constituents of the composite cathode was assessed through a reactivity study using XRD analysis. Ensuring the absence of any chemical reactions between the pore-forming agent and the composite cathode is crucial, as newly formed compounds resulting from such reactions could either insulate or diminish the electrochemical activity of the cathode, as pointed out by Min Fu et. al [19].

Figure 3 displays the XRD pattern of LSCF-BCZY composites incorporating varying amounts of BSW, treated at 1000˚C. As can be seen from the diffraction pattern, only peaks corresponding to LSCF and BCZY constituents are evident, with no apparent impurities present. This observation strongly suggests that the pore-forming agent exhibits chemical compatibility with LSCF-BCZY at 1000˚C. Furthermore, the results indicate complete removal of the pore-forming agent from the cathode material. Essentially, the preservation of phase purity in the composite cathode underscores the potential for maintaining the high catalytic activity of LSCF-BCZY.

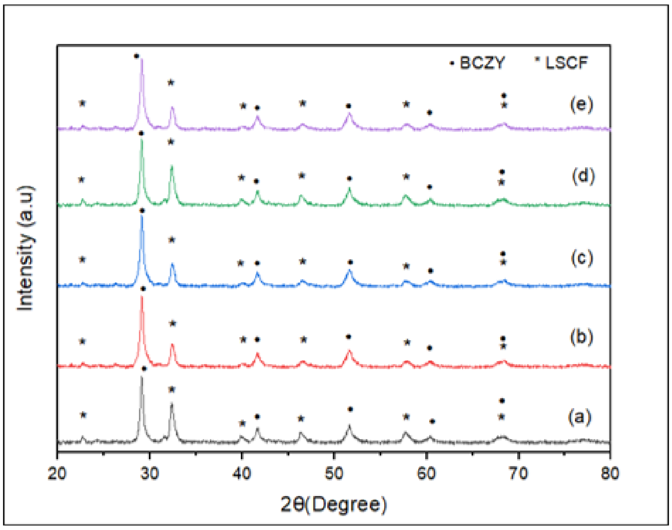

Figure 3. XRD diffraction pattern of (a) unmodified LSCF-BCZY and the composite cathode incorporated with (b) 10 wt. %, (c) 20 wt.%, (d) 30 wt.%, and (e) 40 wt.% of BSW.

3.3. Effect of Different Amounts of Pore Former on the Microstructure of the Composite Cathode

Figure 4 displays scanning electron microscope (SEM) micrographs illustrating composite cathodes incorporated with varying amounts of banana stem waste powder. The images consistently reveal an escalating pattern of porosity as the amounts of banana stem waste powder in the samples increase. This suggests a notable impact of the incorporated pore-forming material on the composite cathode's microstructure, leading to the development of pores that resemble the morphology of the employed pore former.

Figure 4(a) depicts the unmodified cathode, characterized by minimal porosity primarily attributed to micro-fractures resulting from the sample preparation technique. The introduction of 10 wt.% BSW in Figure 4(b) initiates the formation of micropores, evolving into a well-developed porous network at 20 wt.% (c). This trend continues at 30 wt.% (d), where significant porosity and larger pores emerge, likely stemming from the thermal decomposition of BSW and its inherent pore structure (as shown in Figure 2). These elongated pores generally mimic the shape of the pore formers, with their total volume and size scaling proportionally with the BSW content.

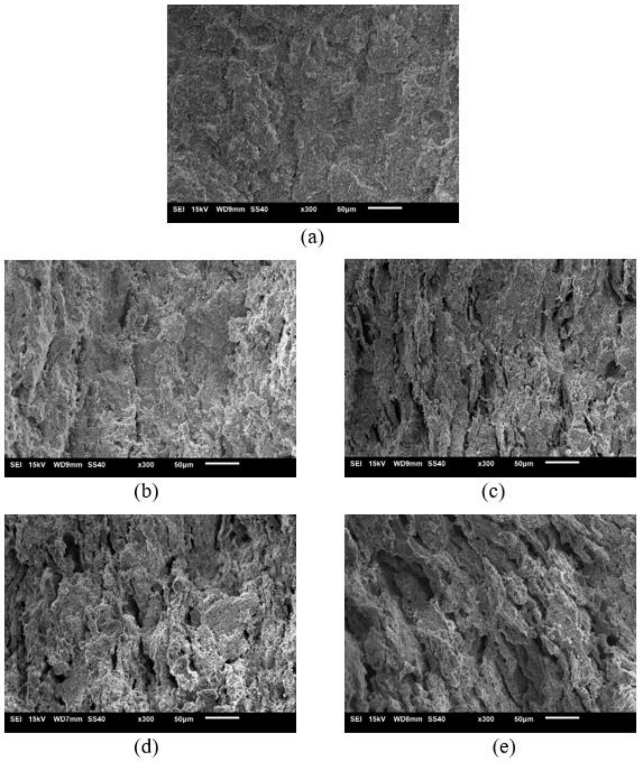

Figure 4. SEM Micrograph of the unmodified composite cathode (a) and the composite cathode modified with (b) 10 wt. %., (c) 20 wt. %, (d) 30 wt. %, and (e) 40 wt. % of BSW.

The 40 wt.% sample presents a complex picture. While offering abundant open pores and promising gas diffusion pathways, the non-uniformity and deformed morphology of these pores raise concerns about their long-term functionality. This phenomenon likely results from the collapse of thin pore walls during high temperature sintering following BSW decomposition. Furthermore, the extensive open porosity, achieved through interconnected passages and streams, enhances gas accessibility but potentially compromises structural integrity. This observation underscores the need for further investigation to optimize BSW loading, mitigate pore deformation, and attain a well-defined porous network that balances performance and durability.

Table 1 illustrates the porosity level of the composite cathode measured by image analysis software, showcasing a progressive increase from 5.53% to 7.10% with the addition of 10 wt.% BSW, further escalating to 25.53% with 30 wt.% BSW. The highest porosity, reaching 32.74%, is observed at 40 wt.% BSW, highlighting a clear correlation between increased amounts of the pore former and higher porosity.

Table 1 Porosity of LSCF-BCZY composite cathode with different amounts of BSW

BSW amount (wt. %)	Porosity (%)
0	5.53
10	7.10
20	11.97
30	25.53
40	32.74

While increased porosity can potentially improve gas diffusion within the cathode layer, it raises concerns regarding possible interruptions in the conducting phase. These interruptions can impede ionic or electronic conduction paths, ultimately diminishing the triple-phase boundary and adversely affecting cell performance.

To evaluate the influence of varying pore former quantities on the physical characteristics of the LSCF-BCZY composite cathode, the densities of the sintered samples at 1000°C were measured and are presented in Table 2. The results demonstrate a consistent reduction in composite cathode density as the amount of incorporated pore former increases. This trend aligns with the findings of Haslam et al. [21], where it was observed that the relative density of the electrode material decreases with higher pore former content. This decrease is attributed to the increase in porosity within the sample's microstructure, leading to greater void spaces and lower overall density.

Table 2 Porosity of LSCF-BCZY composite cathode with different amounts of BSW

BSW amount (wt. %)	Density (g/cm3)
0	1.33
10	1.21
20	1.09
30	0.95
40	0.88

Notably, a linear decrease in sintered sample density is observed with increasing BSW amounts. However, exceeding a pore former content of 30 wt.% leads to increased fragility and susceptibility to cracking, consistent with prior research [20,21]. It's worth noting that excessively high amounts of pore formers, as shown in Figure 4 with 40 wt.% of BSW amount, may lead to the lowest mechanical strength due to the resulting lower sample density of 0.88 g/cm^3. It is crucial to highlight that there exists an upper limit to the quantity of pore former that can be incorporated. Given that low density can negatively impact cathode performance, it is essential to carefully determine the appropriate amount of pore former to achieve the desired density in the composite cathode [6,22].

The findings suggest that an optimal addition of banana stem waste (BSW) is 30 wt.%. This quantity consistently produces cathode porosity within the desirable range of 20 to 30%, in line with previous literature [23]. The scalability of BSW is promising due to its abundant availability and simple processing. Additionally, its properties are adjustable through the manipulation of BSW content and processing methods, allowing for control over pore characteristics such as size and distribution. This tunability offers versatility for various applications. However, challenges related to maintaining consistent BSW properties, including particle size, morphology, and composition, across large batches, may require additional processing steps such as size fractionation or pre-treatment to ensure uniform pore formation. Addressing these challenges is crucial to fully exploit BSW as a sustainable pore former for cathode modification.

For future research, a thorough evaluation of the modified cathode's mechanical and electrochemical properties is necessary. This assessment will provide insights into how the microstructural changes affect the structural integrity and phase conductivity of the composite cathode. Achieving a delicate balance between these factors is critical as it enhances the triple-phase boundary, ultimately improving the performance of the PCFC cathode.

4. CONCLUSION

In conclusion, this study has demonstrated the efficacy of banana stem waste (BSW) as a pore-forming agent in fabricating porous ceramics for protonic ceramic fuel cells (PCFC). The addition of 30 wt.% BSW consistently produced cathode porosity within the desirable range of 20 to 30%, as quantitatively measured in this study. This finding highlights the practicality of using BSW to achieve optimal porosity levels for PCFC operation. Importantly, the use of BSW did not introduce secondary phases, ensuring the uninterrupted electrochemical performance of the cathode. However, the potential variability in BSW quality should be considered, as it could affect the reproducibility and reliability of the results. In addition to assessing mechanical strength and electrochemical performance, future research should focus on mitigating this variability to ensure the consistent performance of BSW as a pore former in PCFC cathodes.

ACKNOWLEDGMENTS

This research was supported by the Fundamental Research Grant Scheme (FRGS/1/2020/STG04/UNIMAP/02/2). The authors thank Universiti Malaysia Perlis for the facilities and support provided.

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