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Muhammad Naufal Amanullah

Diponegoro University

Sulistyo Sulistyo

`sulistyo@lecturer.undip.ac.id`

Diponegoro University

Mohammad Tauviqirrahman

Diponegoro University

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Ball Milling Assisted Homogenization and Particle Size Control of NiO YSZ Anode Materials with Starch Pore Former FOR Solid Oxide Fuel Cell

Muhammad Naufal Amanullah ¹, Sulistyo ^{1*}, Mohammad Tauviqirrahman ¹

¹ Department of Mechanical Engineering, Diponegoro University, Semarang, 50275, Indonesia

*Corresponding author(s). E-mail(s): sulistyo@lecturer.undip.ac.id

Contributing authors: amanullahnaufal@students.undip.ac.id;
mtauviq99@yahoo.com

Abstract

This study investigates the effect of ball milling on the homogenization and particle size characteristics of NiO YSZ anode materials with starch as a pore-forming agent for solid oxide fuel cell applications. The powder mixture was prepared with a NiO YSZ to starch ratio of 70:30 and processed using ball milling at different (BPR), namely 1:10, 1:20, 1:40, and 1:60. The particle size distribution was analyzed using a PSA, while the morphology and elemental distribution were examined using SEM EDX. The PSA results show that the milling process affects the particle size distribution, where the D50 value increases after milling and tends to stabilize at higher BPR. Among the tested conditions, BPR 1:40 provides a more uniform particle size distribution compared to the others. SEM observations confirm that this condition also results in a more homogeneous microstructure with better particle dispersion. Elemental mapping further indicates a uniform distribution of Ni and Zr phases within the anode structure. These results suggest that BPR 1:40 is the most suitable condition for achieving good powder homogenization while maintaining stable particle size characteristics, which is important for improving the microstructure of SOFC anodes.

Keywords: NiO YSZ, ball milling, particle size distribution, SOFC, pore former.

1. Introduction

Solid oxide fuel cells (SOFCs) are electrochemical devices that operate at elevated temperatures and are capable of converting the chemical energy stored in fuels directly into electrical power. This technology is recognized for its high conversion efficiency, relatively low environmental impact, and ability to utilize a wide range of fuels. Owing to these strengths, SOFCs have gained significant interest as a prospective sustainable energy solution, particularly in supporting global efforts toward decarbonization and the transition to cleaner energy systems [1]. SOFCs are well known for its high quality exhaust heat for cogeneration in high temperatures (600-1000°C) [2]. The basic structure of a SOFC cell must include an anode, a cathode, and an electrolyte [3]. Currently, NiO YSZ is widely employed as an anode material. This system offers

strong catalytic activity while preserving good thermal compatibility with other cell components [4]. In planar SOFC configurations, the anode not only facilitates the oxidation of fuel but also serves as the structural backbone of the cell, requiring both mechanical robustness and reliable electrochemical performance [5–10].

Anode performance is strongly influenced by its microstructure, with porosity playing a particularly critical role. Adequate porosity enhances gas diffusion, improves fuel accessibility, and expands the active triple phase boundary (TPB) where electrochemical reactions occur [11–13]. Nevertheless, this parameter must be carefully controlled, as excessive porosity can weaken mechanical integrity, whereas insufficient porosity limits fuel transport and ultimately reduces cell efficiency.

Furthermore, The techniques used in preparing the initial powders as well as the subsequent anode fabrication processes play a crucial role in determining the resulting anode microstructure and the overall performance of the cell. Variations in synthesis routes can significantly influence characteristics such as microstructural features, porosity, particle size distribution, particle morphology, and the length of the triple phase boundary [14]. Various methods have been employed for the synthesis of anode materials, one of which is ball milling.

Although ball milling has been widely employed to improve powder dispersion and reduce particle size in ceramic systems, studies that specifically examine the homogenization of NiO YSZ powders after the addition of starch as a pore forming agent remain relatively limited. In particular, the influence of ball milling on maintaining powder uniformity while controlling particle size in NiO YSZ systems containing pore formers has not been extensively discussed. A clearer understanding of this relationship is important because excessive particle refinement or insufficient mixing may affect the resulting microstructure and ultimately the performance of the anode material. Therefore, this study focuses on the use of ball milling to assist the homogenization of NiO YSZ powders mixed with starch pore former while maintaining appropriate particle size characteristics. The processed powders were subsequently analyzed using a Particle Size Analyzer to determine particle size distribution, while scanning electron microscopy coupled with energy dispersive X ray spectroscopy was used to examine the microstructure and elemental composition. The results are expected to provide insight into how ball milling contributes to powder homogenization and particle size control in the preparation of NiO YSZ anode materials for solid oxide fuel cell applications.

2. Materials and Methods

2.1 Preparation of Anode Supported

NiO-YSZ anode support with a 60 wt %:40 wt % ratio of NiO to YSZ (99%, fuelcellmaterial, Ohio, USA) (12-22 μm), rice strach as pore former (62 μm), and PEG 400 (sigma aldrich, USA) as binder.

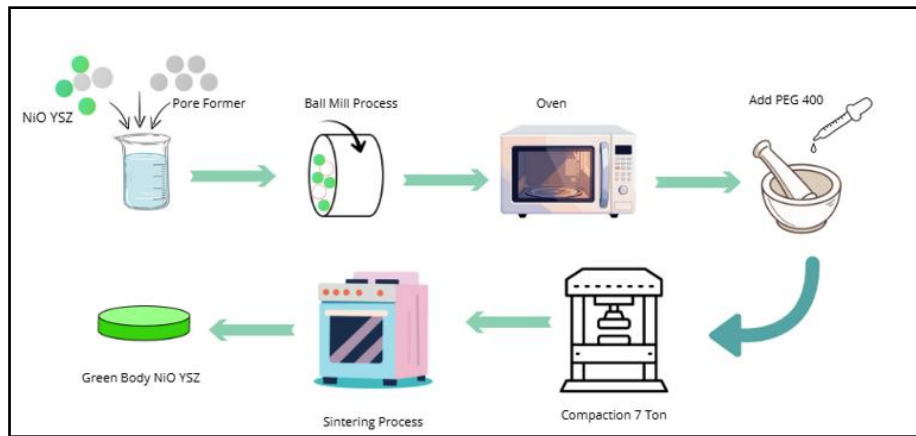


Fig. 1. Schematic of the fabrication process of the green body

Figure 1 illustrates the overall fabrication procedure applied for preparing the anode material in this study. The process began with the preparation of a powder mixture consisting of NiO YSZ and rice starch as a pore forming agent with a mass ratio of 70:30.

The powder mixture was placed into a ball mill jar together with alumina balls (Al_2O_3) with a diameter of 10 mm. Several ball to powder ratios were investigated, namely 1:10, 1:20, 1:40, and 1:60. The mixing process was carried out using a ball milling technique at 150 rpm 6 h in order to achieve a more homogeneous distribution of the starch within the NiO YSZ powder system [15,16]. After the milling stage, the mixed powder was dried in an oven at 100 °C 1 hour to ensure that residual moisture was removed from the powder. Subsequently, polyethylene glycol (PEG) with a concentration of 10 wt% was added as a binder. The powder and binder were manually mixed using a mortar for approximately 15 minutes to obtain a uniform mixture. The resulting powder was then compacted under a pressure of 130 MPa for 15 minutes to form the green anode body [17]. Finally, the samples were subjected to a two step sintering process. The first thermal treatment was conducted at 600 °C with a holding time of 1 hour to remove organic components, followed by a second sintering stage at 1200 °C with a holding time of 4 hours to promote particle bonding and structural stability. The heating rate during the sintering process was controlled at 3 °C/min [17].

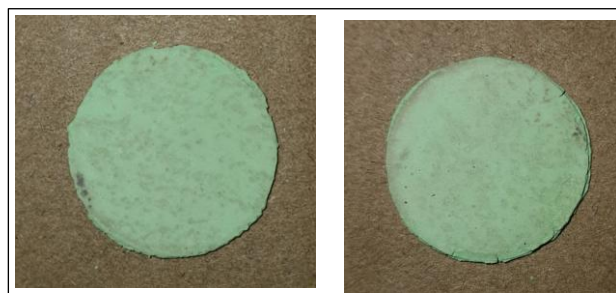


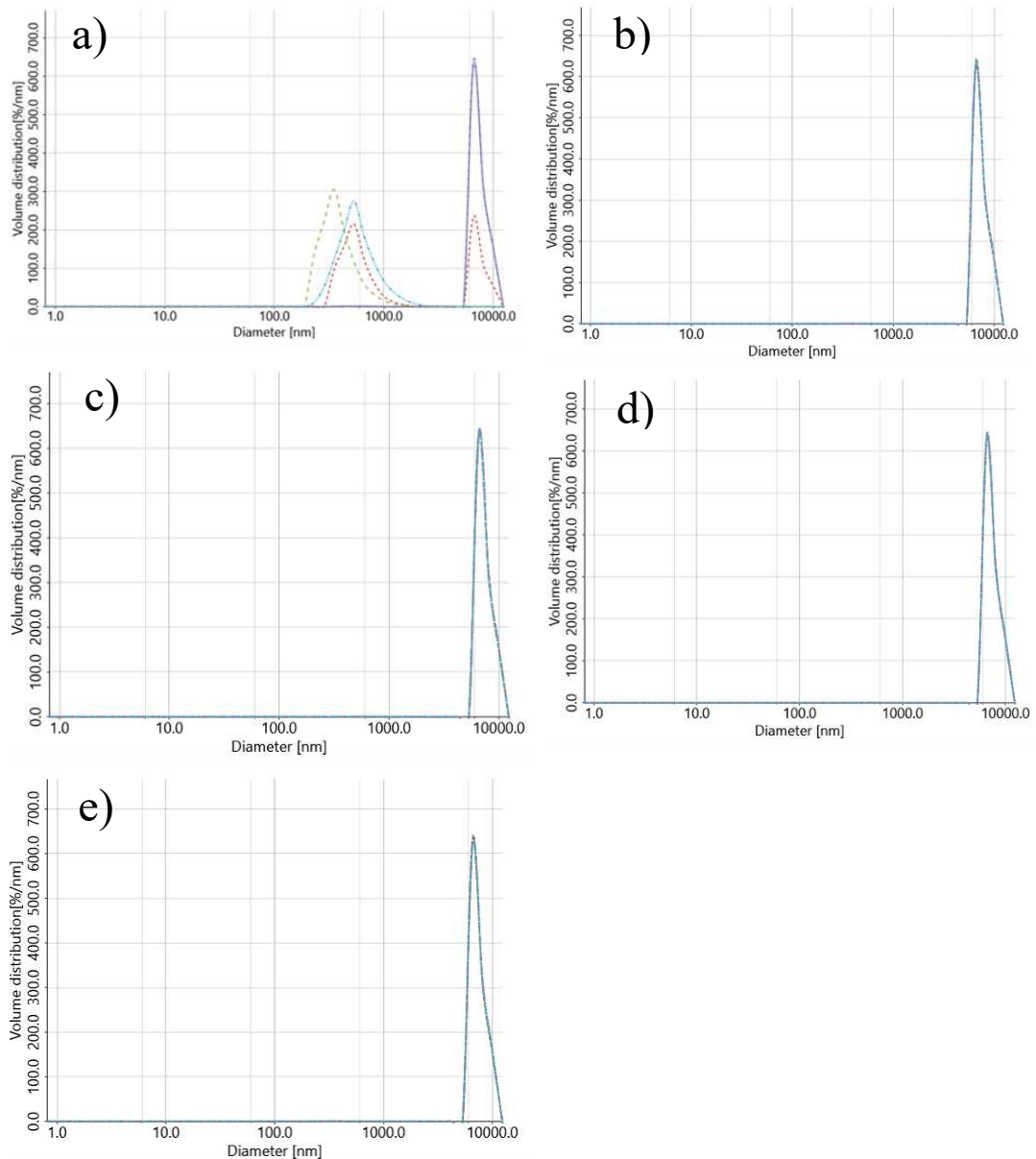
Fig. 2. Green body of the NiO YSZ anode material obtained after sintering

Figure 2 presents the fabricated NiO YSZ samples prepared with different pore former compositions. The samples were produced in a disk shape with an approximate diameter of 25 mm and a thickness ranging from about 1 to 2 mm.

3. Results and Discussion

This section presents the experimental results obtained from the preparation of NiO YSZ anode materials with starch pore former using the ball milling method. The discussion focuses on evaluating the influence of the ball to powder ratio on the homogenization behavior and particle size characteristics of the prepared powders. Particle size distribution was analyzed using a PSA, while the microstructural features and elemental composition of the samples were examined through SEM coupled with EDX. These characterizations were carried out to provide a clearer understanding of how the milling conditions affect particle size control and the resulting microstructure of NiO YSZ anode materials for solid oxide fuel cell applications.

3.1 Particle Size Analyzer



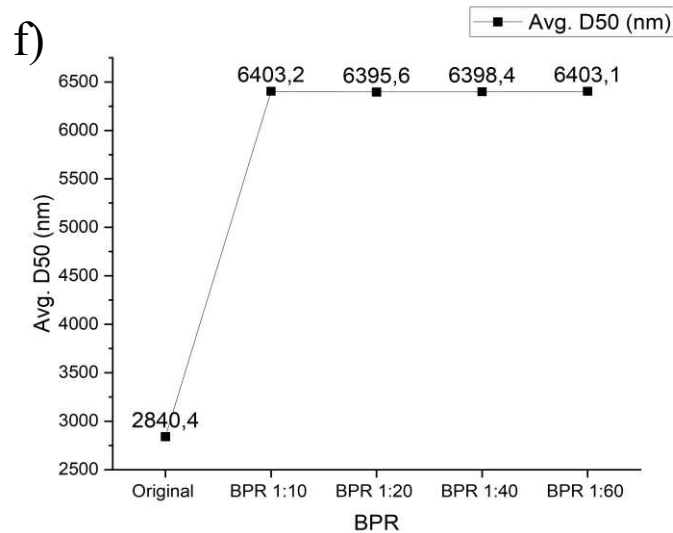
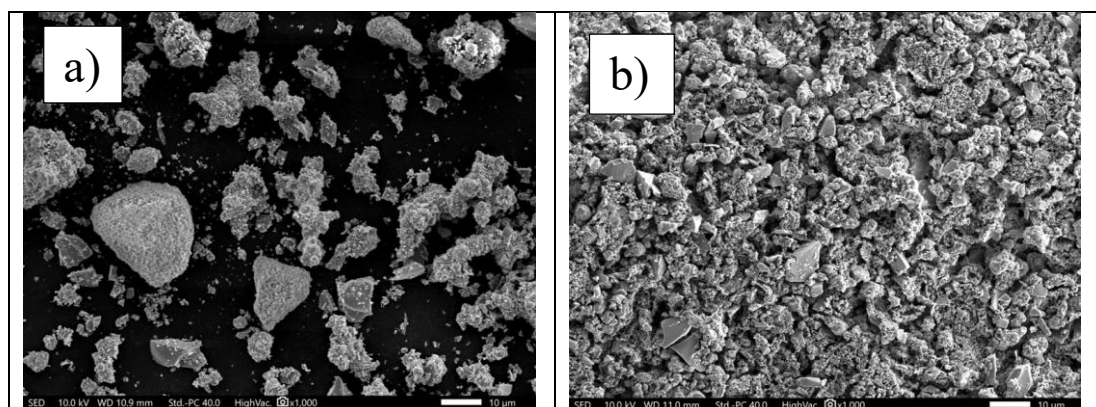


Fig. 3. PSA test results: **(a)** original sample, **(b)** BPR 1:10, **(c)** BPR 1:20, **(d)** BPR 1:40, **(e)** BPR 1:60, and **(f)** comparison of the average D50 values.

The Particle Size Analyzer (PSA) results in Figure 3 show that the milling process has a clear effect on the particle size distribution. The median particle size (D50) increases from 2840.4 nm in the initial sample, even though the starting powder is relatively coarse at around 62 μm , to approximately 6400 nm after milling. This indicates that the change in particle size is strongly influenced by the milling parameters, especially BPR. Although the D50 value at BPR 1:20 is slightly lower than that at BPR 1:40, the difference is very small, suggesting that the system has reached a relatively stable condition where increasing the milling intensity no longer significantly changes the median particle size. Instead, the effect of BPR is more visible in the distribution profile, where BPR 1:40 tends to show a more consistent and uniform particle size distribution

3.2 Scanning Electron Microscopy (SEM)



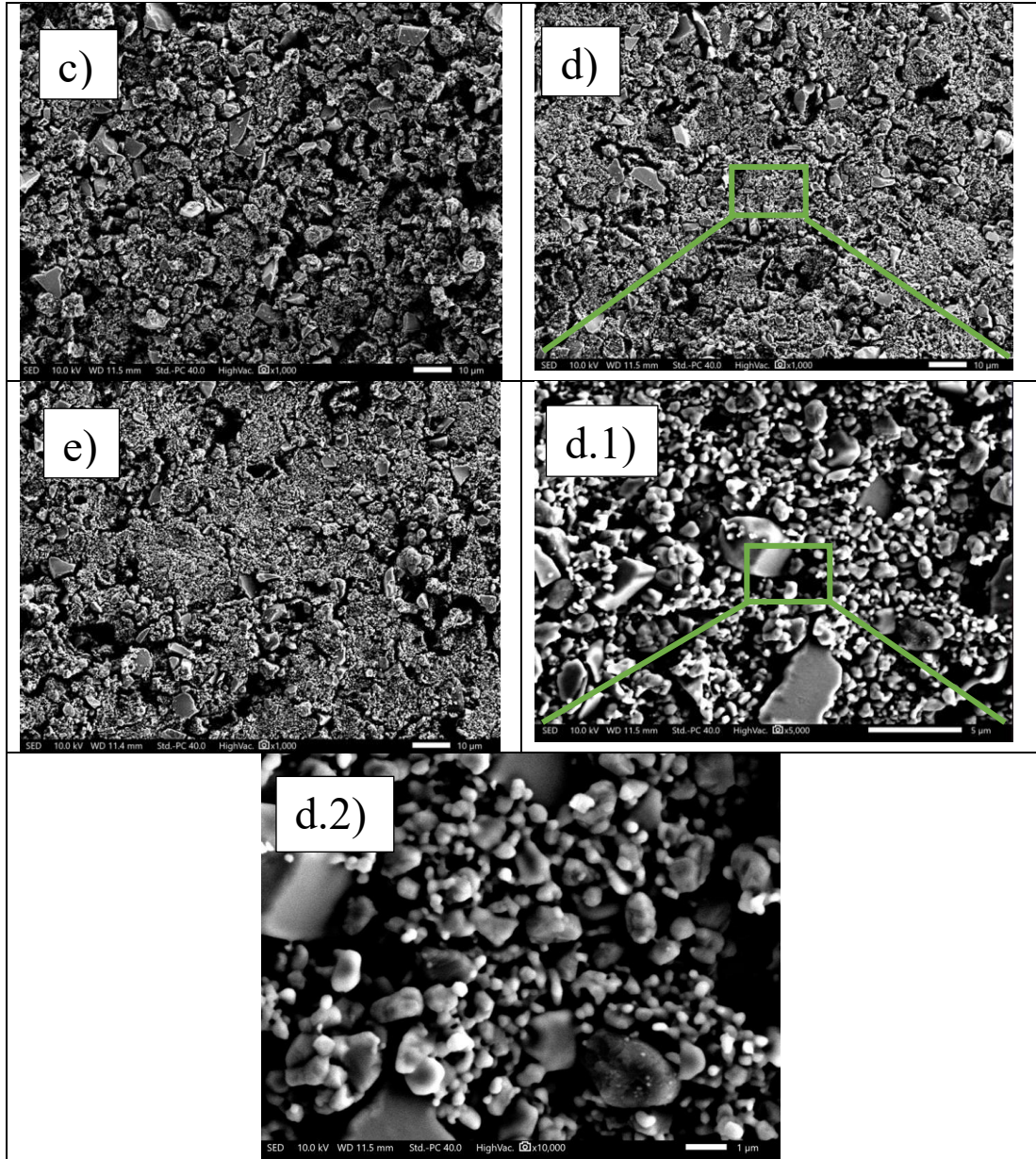


Fig. 4. SEM images of powders at different BPRs: (a) initial (1000×), (b) 1:10 (1000×), (c) 1:20 (1000×), (d) 1:40 (1000×), (d.1) 1:40 (5000×), (d.2) 1:40 (10,000×), and (e) 1:60 (1000×).

The SEM (JSM-IT 200 JEOL Ltd., Japan) with EDX observations presented in Figure 4 demonstrate that the ball to powder ratio (BPR) significantly influences the morphology and homogeneity of the NiO YSZ mixture with starch as a pore former. The initial powder (Fig. 4a) exhibits large, irregular particles with poor distribution, indicating the absence of effective mixing. At lower BPR values of 1:10 and 1:20 (Figs. 4b and 4c), particle size reduction begins to occur; however, noticeable agglomeration remains, suggesting that the milling energy is still insufficient to achieve uniform dispersion. A more homogeneous microstructure is observed at BPR 1:40 (Fig. 4d), where particles appear finer and more evenly distributed, as further confirmed by higher magnifications (Figs. 4d.1 and 4d.2). This condition indicates that the applied milling energy is optimal for breaking agglomerates and promoting uniform mixing between NiO, YSZ, and the pore forming agent. In contrast, at BPR 1:60 (Fig. 4e), excessive milling energy tends to induce re agglomeration of fine

particles, leading to less uniform structures. Therefore, BPR 1:40 is considered the most suitable condition for achieving homogeneous mixing, which is essential for enhancing the triple phase boundary (TPB) in SOFC anodes. This finding is consistent with previous studies reporting that appropriate milling conditions improve particle dispersion and interfacial contact in NiO YSZ systems, thereby enhancing microstructural uniformity and electrochemical performance [18].

3.3 Energy Dispersive X-Ray Spectroscopy (EDX)

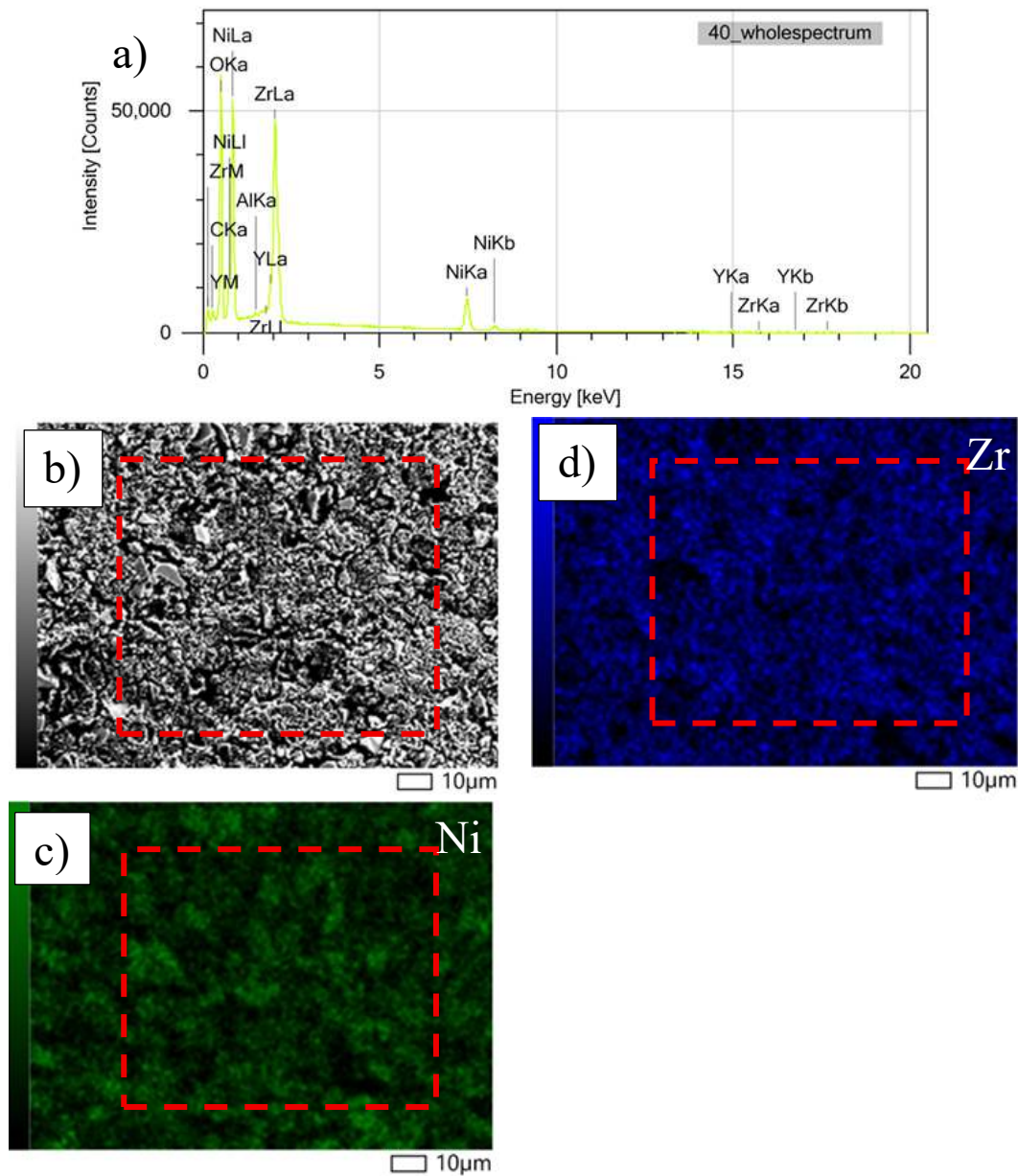


Fig. 5. SEM–EDX analysis of the sample BPR 1:40: (a) EDX spectrum indicating the detected elements, (b) SEM micrograph of the analyzed region, (c) elemental mapping of Ni distribution, and (d) elemental mapping of Zr distribution.

Figure 5 presents the SEM–EDX characterization of the NiO YSZ anode prepared with flour as a pore-forming agent at a BPR ratio of 1:40. The EDX spectrum in Fig. 5(a) confirms the presence of the primary elements forming the anode material,

including Ni, Zr, Y, and O, which correspond to the NiO phase and yttria stabilized zirconia (YSZ) ceramic matrix. The detected peaks indicate that the composite electrode was successfully synthesized without the formation of unexpected dominant impurity phases. The SEM micrograph shown in Fig. 5(b) reveals a relatively porous and heterogeneous surface morphology within the analyzed region, which can be attributed to the thermal decomposition of the flour pore former during the sintering process, resulting in the formation of micro-voids that are beneficial for gas diffusion in SOFC anodes. Furthermore, elemental mapping analysis illustrates the spatial distribution of Ni and Zr within the electrode structure, as shown in Fig. 5(c) and Fig. 5(d). The Ni mapping demonstrates that the nickel phase is dispersed throughout the observed area, forming an electronic conduction pathway within the anode matrix. Meanwhile, the Zr distribution represents the YSZ phase acting as the ionic conductor. The relatively uniform dispersion of both elements suggests that the powder mixing and compaction processes produced a homogeneous composite structure, which is essential for maintaining effective triple phase boundaries where electrochemical reactions occur in SOFC electrodes. Similar microstructural characteristics have been reported in previous studies, where the coexistence and connectivity of Ni and YSZ phases play a crucial role in determining the electrochemical performance of the anode material [19].

4. Conclusion

The results of this study confirm that the ball milling process has a significant influence on the particle size characteristics and homogenization behavior of NiO YSZ anode materials with starch as a pore forming agent. The particle size analysis shows that the median particle size increases after milling and tends to stabilize as the ball to powder ratio becomes higher, indicating that further increases in milling intensity do not significantly change the overall particle size. Among the investigated conditions, the ball to powder ratio of 1:40 provides the most consistent particle size distribution. This result is in agreement with the microstructural observations, where a more uniform and homogeneous particle arrangement is obtained at the same condition. The elemental analysis further confirms that the nickel and zirconium phases are well distributed within the material, indicating effective mixing during the milling process. Based on these findings, the ball to powder ratio of 1:40 can be considered the most suitable condition for achieving good homogenization and stable particle characteristics, which are important factors in supporting the development of high performance anode materials for solid oxide fuel cell applications.

CRedit authorship contribution statement

Muhammad Naufal Amanullah: Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Visualization, Writing original draft. **Sulistyo:** Supervision, Validation, Writing review & editing. **Mohammad Tauviqirrahman:** Conceptualization, Methodology, Supervision, Validation, Writing review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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