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A Brief Review on Recent Advancement of Anode Materials for Biogas-Fed Solid Oxide Fuel Cells (SOFCs)

S. Islamiyah[1*], A Nandini[1]

[1]Department of Chemical Engineering, Faculty of Engineering, University of Pembangunan National Veteran Jawa Timur, 60294, Indonesia

*Corresponding e-mail: syuaibatul.tekkim@upnjatim.ac.id

Abstract. Solid Oxide Fuel Cell (SOFC) is a fuel cell technology run at high temperatures which enable internal reforming of fuel and production of high-quality by-product heat for cogeneration. The most distinguished advantage of SOFC is its excellent fuel flexibility. Biogas is one of the alternative fuels to preferable pure hydrogen. One of the important issues in operating SOFC with biogas is the formation of carbon on anode surface. Therefore, the development of coking-resistant anode materials is essential to create a high performance and stable biogas-fed SOFC. This review provides a brief survey on the recent progress of anode materials, mainly Ni-based cermet, and the modifications to prevent carbon deposition. The current situation of biogas production and utilization in Indonesia is also briefly reviewed.

Keyword: Solid Oxide Fuel Cell; Anode; Biogas

1. Introduction

The excessive use of fossil fuels is one of the main causes of Green House Gases (GHG) formation and the instability of the energy price. Various renewable energy resources are being researched as the possible substitute for fossil fuels, including solar, tidal, and wind energy, but the fluctuated production of their powers limit the energy supply. In this regard, one practical and promising method for the near future is energy conservation which is to increase the current energy conversion efficiency rather than unlimited use of intermittent alternative energy. In this regard, the fuel cells (FCs) technology is highly anticipated [1].

A fuel cell (FC) is a clean and efficient device to convert the chemical energy of fuels such as hydrogen and hydrocarbons into electrical energy with very high efficiency (>60%) compared to the established technology of the internal combustion engine (ICE). One main advantage of fuel cells is their fuel flexibility. Because of its high reactivity for the electrochemical anode reaction and the fact that its oxidation produces water, hydrogen is preferred in many types of fuel cells. However, since hydrogen does not naturally exist as a gaseous fuel, it must often be produced from a fuel source that is readily available in the area for viable fuel cell systems to function [2]. To address the problems associated with hydrogen production, storage, and transport, alternative fuels are considered.

Biogas is promising alternatives among available fuel options due to its accessibility, affordability, and potential as a distributed energy source [3]. Anaerobic digestion (AD) is a common method used in rural communities of developing country to produce biogas, which can then be used as a source of energy. However, because of the high amount of CO_2 dilution and the fuel's low calorific value, it cannot be used in conventional burners or heat engines [4]. Solid-oxide fuel cells (SOFCs), with its fuel flexibility, can use biogas directly and with little pre-treatment. SOFCs employ both CH_4 and CO_2 contained in biogas to create a syngas (CO+ H_2) combination with a higher energy content, which further are oxidized to produce electricity, via internal dry reforming [5].

Since SOFCs fed by biogas are still in their early-stage research compared to SOFCs fed by pure hydrogen, extensive research is necessary to explore and further develop new materials that enable a stable operation with high output. This review aims to summarize the recent development of anode materials used in biogas fed SOFC and discuss the problem associated when using biogas as fuel in SOFCs, as well as present solutions offered by researchers. In addition, the feasibility of integrating SOFC system to electricity generation in Indonesia is also concluded.

2. Biogas in Indonesia

Biogas is a fuel derived from biomass source commonly through anaerobic digestion (AD). The digestion of organic material in biomass involving microbes and occurs in four steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis [6]. Methane, carbon dioxide, and trace amounts of nitrogen and hydrogen make up the majority of biogas [7]. It can be used to generate electricity and heat as well as to power a gaseous car. By using biogas, an effort is made to both reduce GHG emissions and increase the economic value of waste as a source of energy [8].

Figure 1 illustrates how various biogas applications provide flexible means of producing the necessary energy for the industrial or social sectors. The primary uses of biogas are in combined heat and power (CHP) facilities, hydrogen production facilities, and advanced energy systems like fuel cells. [9].

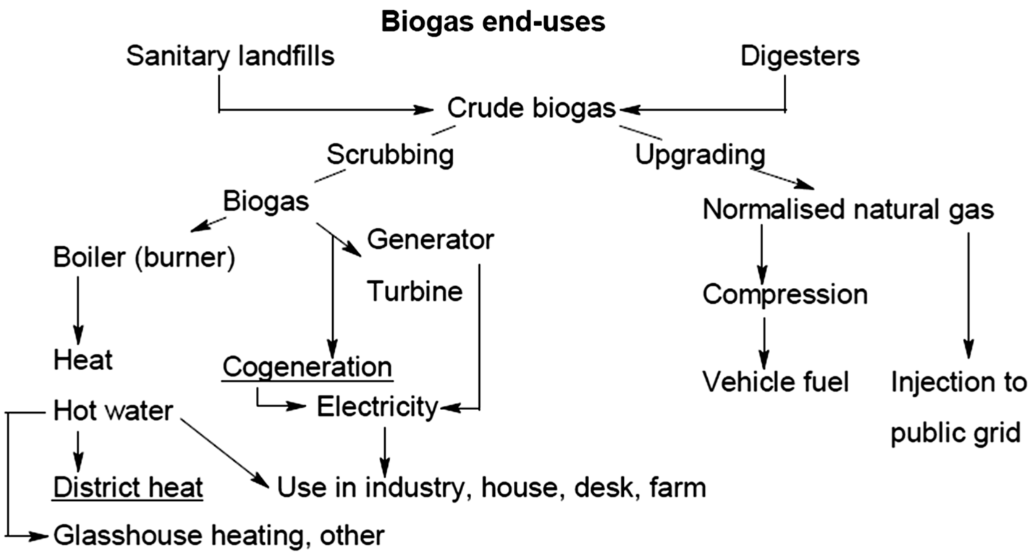

Figure 1. The overview of biogas utilization

The biogas contains 55 to 70% methane, 30 to 45% carbon dioxide, and other trace gases such as oxygen, carbon monoxide, and hydrogen sulfide [10]. To obtain biogas from the biomass source, the organic waste should be placed in an oxygen-free area. The organic matter in the waste will break down and create biogas. Because the carbon in biogas is derived from organic waste that has fixed atmospheric carbon dioxide, it is considered as carbon neutral energy source. Organic trash is also highly sustainable because it will continue to grow and be available as long as the humankind exists.

Animal farms, municipal solid waste, agricultural residues, industrial sludge, and wastewater treatment plants are all sources of the numerous feedstocks used to produce biogas. Muzenda (2014) identified suitable biomass for biogas production (i.e., food waste, manure, crop residue, abattoir waste, and stillage). Food waste was shown to have a high potential as a biogas feed source since it contains proteins, lipids, carbs, and trace components that encourage a balanced process. Biomass with a high fat content has the greatest potential for biogas production [11].

By 2025, the Indonesian government plans to incorporate 23% share of renewable energy in their energy supply. In case of biogas, by 2015, 16,000 biogas plants had been installed across ten provinces in Indonesia [12]. Most biogas production case studies in Indonesia are currently conducted on a small scale with animal waste as a potential feedstock. Various feedstocks, from municipal solid waste to human excreta, were then also being explored to evaluate the viability of producing biogas in Indonesia [13–16]. The biogas produced is concentrated on being utilized directly for home activities, such as cooking and water heating, as the majority of biogas facilities are located in rural regions. There are initiatives, however, to improve the quality of the biogas generated by these facilities using purifying techniques, such as pressurized gas scrubbing [17].

3. Solid Oxide Fuel Cell (SOFC)

SOFC is a fuel cell technology that often runs at high temperatures. It is excellent for use in big, high-power applications, including major industrial facilities and power plants. SOFC systems typically run at very high temperatures (600–1000°C) and employ solid ceramics as electrolytes. The high operating temperature allows internal reformation of the fuel, which also encourages quick electrocatalytic reactions with base metals and generates high-quality by-product heat for cogeneration. This kind of fuel cell's efficiency can increase to 70%.

Three primary parts make up a solid oxide fuel cell: anode, cathode, and a dense electrolyte. The operating principles of a typical oxygen-ion conducting electrolyte SOFC are depicted in Figure 2. The anode receives fuel, such as H_2 or hydrocarbon, and the cathode receives oxygen from the air. At the cathode side, oxygen is converted to O^{2-} and transferred via the electrolyte to the anode in order to produce electricity. By way of an external pathway, the free electrons generated by the oxidation reaction at the anode then move to the cathode. The SOFC obviously does not burn fuel, which automatically prevents the Carnot cycle, which is why it has a higher electrical efficiency than traditional power generators.

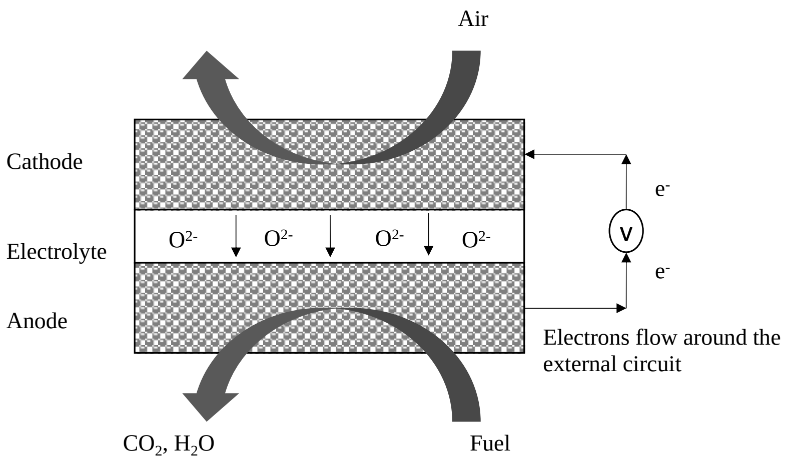

Figure 2. The schematic working principle of SOFC

The reduction of hydrogen and oxidation of oxygen at the anode and cathode sides respectively are shown below [18]

Anode	:	$H_2 + O^{2-} \rightarrow H_2O + 2e^-$
Cathode	:	$1/2O_2 + 2e^- \rightarrow O^{2-}$
Overall	:	$H_2 + 1/2O_2 \rightarrow H_2O$

When using biogas, the main reactions are steam reforming and dry reforming as shown below

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (1)$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad (2)$$

In addition to dry reforming reactions, there are other reaction paths, such as the water gas shift reaction.

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (3)$$

The water-gas shift equilibrium can be pushed in either direction depending on the reaction conditions. The predominant reactions in fuel cell systems depend on the temperatures, gas concentrations, and system configuration [19]

Biogas are oxidized with oxide ions at the anode in SOFC. Strong electronic conductivity and higher resistance to carbon deposition are especially important requirements for the anode material. Recently, various research projects have shifted their focus to the direct use of biogas in SOFC systems, and as a result, attention has been put into developing coking-resistant anode materials. The majority of the anode materials utilized in biogas-fed SOFC today are nickel-based anodes. The following section will discuss more details on anode materials used in biogas fed SOFCs to date.

4. Anode Materials used for biogas fueled SOFC

Most current research on SOFC powered by biogas focuses on Ni-based anodes. This is due to Ni's dual function, which is a good catalyst for producing C-C bonds and breaking C-H bonds. However, coking resistance has to be improved with specific, focused modifications. [20]. Nickel oxide-YSZ (NiO-YSZ) or nickel oxide-GDC (NiO-GDC) are commonly used composite materials in state-of-the-art SOFC. This type of electrodes is called composite electrode and mixed ionic and electronic conducting materials (MIECs). The mixed conductivities are especially beneficial since they can facilitate more triple-phase boundaries (TPBs) formation, an area in which the fuel, anode and electrolyte come into contact. These advantages of composite electrodes enhance catalytic processes generally, as well as the lifetime and electrochemical performance of the fuel cell stack at the device level [9–11]. However, Ni-YSZ is prone to coking and deactivation by other pollutants when hydrocarbon is used as fuel in SOFC. Researchers have been exploring various scenario to suppress the coking on the anode's surface.

Ma et al. infiltrated $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BCZYYb) into Ni-YSZ anode. This strategy significantly enhanced the electrochemical performance of the cells. A maximum power density of 1.43 W cm^{-2} at 750°C was yielded and the cell remained stable after 50 hours operation. Different current loads were used to investigate the most common reactions, and the result suggested that reforming methane without carbon formation was the dominant reaction [19]. The modification of Ni-YSZ with TiO_2 also shows improved peak power density at 850°C with less carbon deposition after 40 h operation. The TiOx powder that is reduced under high-temperature infrared light excitation produces hydroxyl radical, and it is believed to be the possible factor for the modified anode's high activity and resistance to carbon deposition [24].

Another anode material that has been extensively researched is Ni-GDC. Saadabadi et al. investigated a Ni-GDC anode under different ratios of CH_4/CO_2, or commonly annotated as (R). The study reveals that the cell performance is dependent on R value. When $R \leq 1$, a stable cell performance has been attained, and when $R > 1$, coking is noticed. $R = 1$ produced the best results because there was the least amount of deterioration and the most amount of power generation [25]. To inhibit the graphitic carbon deposition, Au was incorporated into Ni-GDC. The result shows although carbon deposit was observed, it did not hinder the electrochemical performance of the cell under closed-circuit condition. The reactions involved in preventing carbon deposition under closed-circuit operation are as follows [26]:

$$C(s) + O^{2-} \rightarrow CO + 2e^- \quad (4)$$

$$C(s) + 2O^{2-} \rightarrow CO_2 + 4e^- \quad (5)$$

Ni-ScSZ is also actively researched as an alternative to Ni-YSZ anode. The experiment by a research group in Kyushu University reveals severe coking was observed when using actual biogas as a fuel. The H_2S contamination of the actual biogas might lead to this carbon formation. They found that the air addition to the actual biogas could lower the possibility of carbon deposition and allowed SOFC to operate more steadily [27]. The coke formation is less expected when doping tin (Sn) to Ni-ScSZ anode. However, while the electrochemical performance of the cell improved, higher deposited carbon was detected on the doped anode compared to the pristine one. Although the carbon deposition did not impede the electrochemical performance, it can further lead to breaking of the anode, so it should be prevented. [28]. Other anode materials used to operate biogas fed SOFC is listed in Table 1.

Table 1. The list of anode materials used in biogas fed SOFC

Anode	Operating Temperature (°C)	Fuel	Ref.
$BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BCZYYb) infiltrated Ni-YSZ	750-850	simulated biogas ($CH_4/CO_2/H_2O/H_2/CO$=36/36/20/4/4%)	[19]
TiO_2 modified Ni-YSZ	850	simulated biogas (R=2.3)	[24]
Ni-GDC	800-900	simulated biogas (R= 0.6-1.5)	[25]
Ni(Au)-GDC	640	Simulated biogas (R=1)	[26]
NMO coated GDC and NiO	500-700	wet CH_4	[29]
Cu impregnated NiO-GDC	610	simulated biogas	[30]
Ni-ScSz	800	actual biogas	[27]
Sn-Ni-ScSz	750	dry biogas	[28]
Ni-CGO Co-Ni-CGO Cu-Ni-CGO	400-800	simulated biogas (R=1)	[31]
Mo-Ni-CeO_2	750	simulated biogas ($CH_4/CO_2/H_2$=70/25/5%)	[32]

5. Conclusion

In terms of versatility to operate with diverse fuel combinations, SOFC systems are promising technologies for electricity generation. Biogas is a intriguing fuel option that should be researched. Furthermore, the existing high CO_2 concentration available could favor direct internal methane reforming. The potential to use SOFC in generating electricity from biogas in Indonesia is huge. The utilization of biogas in Indonesia now is mostly for household purposes such as cooking. Learning from Malaysia, integrating SOFC into anaerobic digester could yield 76.95% higher performance than the conventional biogas-based electricity generation.

To date, Ni-based anodes are still the most extensively researched with some modifications to hinder the coke formation. The extensive development of anode material for biogas-fed SOFC has promised more possibilities in realizing the application of SOFC technology for generating electricity, especially in rural areas. SOFC is a complex system, so more research must be carried out to understand all reactions and mechanisms involved to yield higher power output. In addition, a study on the possible application of biogas-fed SOFC in Indonesia could be one of the areas of interest since there needs to be more studies in this area.

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