

Effect of syngas and coal composition on performance of solid oxide fuel cell

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ABSTRACT

Gasification technology includes the conversion of fossil fuels into either combustible gas or synthesis gas (syngas) for subsequent utilization. It finds its applications in the production of clean power as well as chemicals. Coal is one of the world's important sources of energy fueling around 40% of the power stations around the world. It is commonly agreed that coal pits will be mined more intensively and in more numbers in the coming years and that lignite and hard coals will be the major energy suppliers until 2100. Integrated gasification fuel cell hybrid power generation system is a promising system for coal utilization. It combines clean coal gasification technology with high efficient fuel cell technology. In this paper, effect of syngas and coal composition on performance of solid oxide fuel cell was studied. It was observed that different ratios of H₂ and CO affect the current and voltage of fuel cell. With higher molar fraction of H₂ the better output voltage was obtained under the same working conditions. The trace species in coal also affect the performance of solid oxide fuel cell. Ni, Be, Cr, K and Na trace species present in coal also affect the performance to some extent.

Key Words: syngas; coal gasification; solid oxide fuel cell; performance.

INTRODUCTION:

Power industry due to present environmental and economic condition is bound to look other methods of production such as clean coal and renewable energy. Hydroelectric, Solar, and wind power require greater expense to make it functional. Coal is considered to be the most economical and beneficial for clean power generation with the new gasification technology. Raw coal syngas directly derived from gasification system has compositions varying significantly with the rank, composition and the origin of the coal and thereafter specific gasification processes [1,2]. Integrated gasification fuel cell (IGFC) hybrid power generation system is the optimal method of coal utilization [3].

Solid oxide fuel cell (SOFC) will play vital role in clean power generation due to its efficiency and no emission of Gases. One of big advantages of SOFC is that external driven fuel enhances its potential. Various contaminants have adverse effects on SOFC Anode and decrease cell performance [4]. Three types of gasification i.e. moving bed, fluidized-bed, and entrained bed depend on gasification produces the most H₂ and CO at temperature greater than 1200°C [5]. Phosphides and phosphates in the nickel catalyst cause most degradation [6]. Ag is not commonly used at anode [7] as nickel has higher catalytic activity at high melting point and cheaper. To make SOFC cost and time efficient smaller fuel cell used by current collecting mesh. Ag used at the mesh at the cathode also due to its electronic conductivity and lower cost [8-10].

In the gasifier, a slurry of coal and water is converted to syngas, a mixture of H_2 , CO , H_2O , CO_2 , and gaseous impurities such as N_2 , Ar , HCl , H_2S , COS , NH_3 , Hg , and CH_4 . The composition of the produced syngas is a function of the composition of coal feed, and the gasification conditions (especially the ratio between oxygen or air and steam used as the gasifying agents). During gasification of coal, volatile contaminants usually form that results in increasing ohmic and electrochemical losses [11]. Syngas from coal gas can be used in SOFC thus reduce harmful emission and increase efficiency up to 60% in integrated fuel cell based power production system (IGFC) as shown in Fig. 1 [12]. Four major components CO , H_2 , CO_2 and H_2O consist of 90% of contents in Coal Syngas [13].

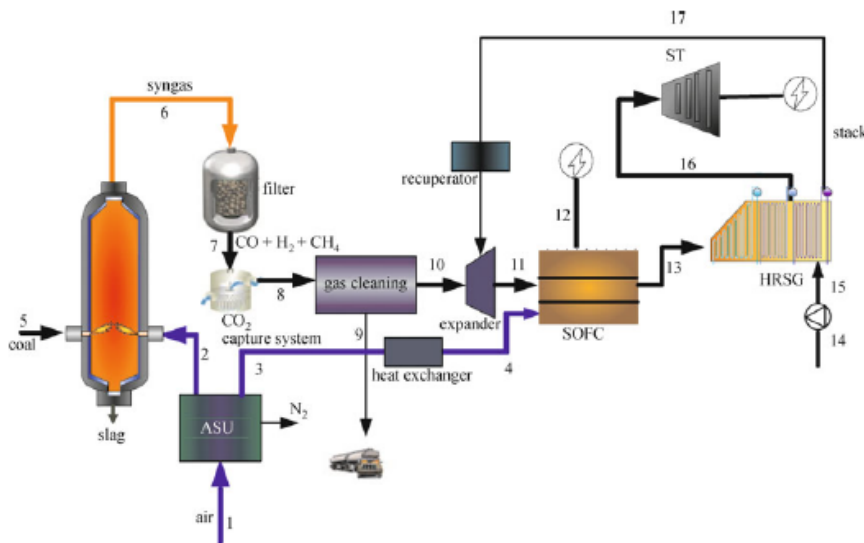


Fig. 1: Simplified flow diagram of the integrated SOFC model in the IGFC plant

The conditioning of the raw gas is challenging, as it might contain an unacceptable amount of contaminants [14]. If the concentration of hydrocarbons and tar is high a subsequent reforming step can also be necessary. Traces of Impurities such as S, Cl, P, As that may present in syngas, cannot be removed in Gasification process. Gas cleaning will involve several steps, e.g. removal of alkali metals and particulates, sulphur and ammonia. Be, Cr, K, Na, V, and Z trace species can also form condensed phases and should not affect SOFC anode performance. The objective of this study is the review of the effect of syngas composition from gasification process on performance of SOFC.

The composition of the produced syngas is a function of the composition of coal feed, and the gasification conditions (especially the ratio between oxygen or air and steam used as the gasifying agents). Tar (heavy hydrocarbons) are unwanted side products in gasification, and some CH_4 (2–12%) and C_2 's (0–6%) are usually found in the syngas. High concentrations of CH_4 will lead to efficiency losses in downstream syngas conversion processes. The conditioning of the raw gas is challenging, as it might contain an unacceptable amount of contaminants [14]. If the concentration of hydrocarbons and tar is high a subsequent reforming step can also be necessary. Gas cleaning will involve several steps, e.g. removal of alkali metals and particulates, sulphur and ammonia. Be, Cr, K, Na, V, and Z trace species can also form condensed phases and should not affect SOFC anode performance. The objective of this study is the review of the effect of syngas composition from gasification process on performance of SOFC.

DISCUSSION

1. Effect of H₂ and CO concentration

With the different relationships between reaction equilibrium constants and temperature, the molar fractions of species change differently (Fig. 2). Current-Voltage (V-I) characteristics measurements showed that use of CO-rich fuel gases results in comparable performance to that of H₂-rich gases and the V-I characteristics depend on composition of carrier gas. Change in cell voltage caused by varying fuel composition was mainly caused by the change in anode impedance. The H₂-to CO ratio was varied from H₂ fuel (H₂:CO = 10:0) to CO fuel (H₂:CO = 0:10) as shown in Fig. 3. The higher molar fraction of H₂, between H₂ and CO applied as fuel, resulted in better output voltage under the same working conditions. As Fig. 2 shows, CO joins in the electrochemical reaction and water shift reaction as well. So the molar fraction of CO is decreasing gradually and CO₂ is increasing by about 26.3% according to these two reactions under the working conditions. In the outlet region, hydrogen is nearly exhausted and the molar fraction of CO decreases by about 25%. Thus, the outlet gas in anode contains little hydrogen, 13.7% carbon monoxide, 37.9% carbon dioxide, and 47.5% water steam. As the equilibrium constant of water gas shift reaction reduces with the temperature increasing, the decrement of molar fraction of hydrogen is larger than that of carbon monoxide with the reactions processing under the calculation conditions.

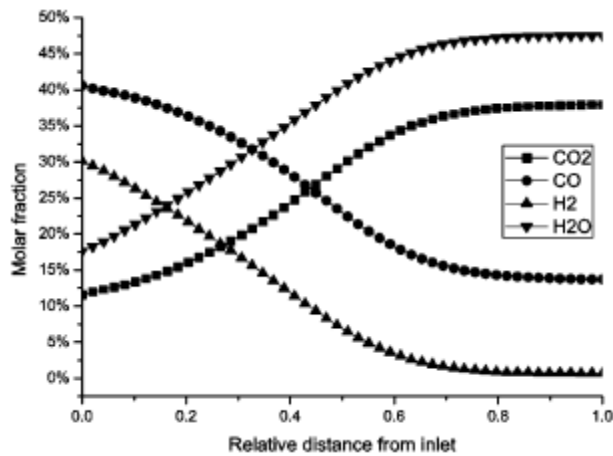


Fig.2: Distribution of species along anode

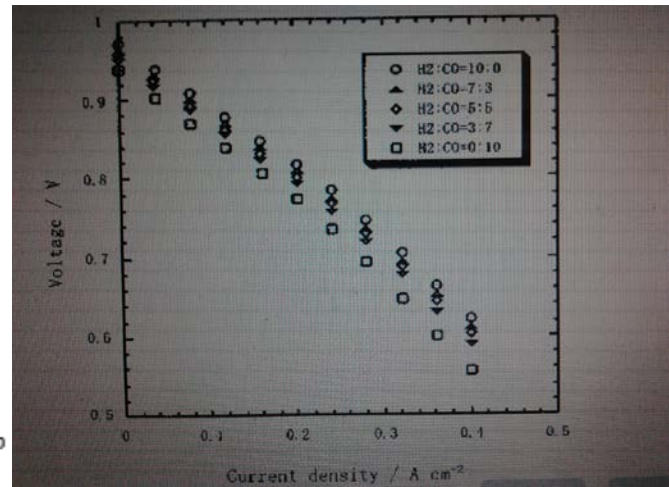


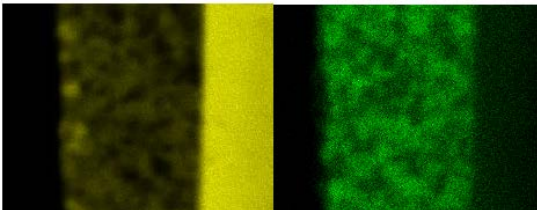
Fig.3: V-I characteristics for H₂&CO ratios

2. Effect of Phosphorus

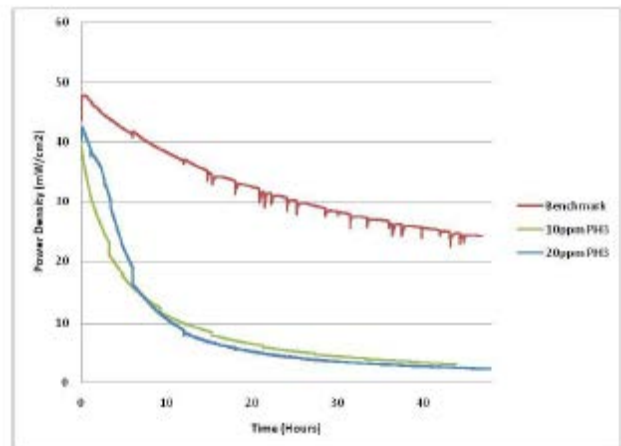
The interaction of phosphorus in synthetic coal gas with the nickel-based anode of solid oxide fuel cells has been investigated. Tests with both anode-supported and electrolyte-supported button cells were performed at 700 to 800°C in synthetic coal gas containing 0.5 to 10 ppm phosphorus, which was introduced as phosphine. Two primary modes of degradation were observed. The most obvious was the formation of a series of bulk nickel phosphide phases, of which Ni₃P, Ni₅P₂, Ni₁₂P₅ and Ni₂P were identified. Phosphorus was essentially completely captured by the anode, forming a sharp boundary between converted and unconverted anode portions. These products partially coalesced into large grains, which eventually affected electronic percolation through the anode

support. From thermodynamic calculations, formation of the first binary nickel phosphide phase is possible at phosphorus concentrations < 1 ppb in coal gas at typical fuel cell operating temperatures. A second mode of degradation is attributed to surface diffusion of phosphorus to the active anode/electrolyte interface to form an adsorption layer. Direct evidence for the presence of such an adsorption layer on nickel was obtained by surface spectroscopies on fracture surfaces. Further, cell performance losses were observed well before the entire anode was converted to bulk nickel phosphide. Impedance spectroscopy revealed that these losses were primarily due to growth in electrodic resistance, whereas large ohmic increases were visible when the entire anode was converted to nickel phosphide phases. The rate of resistance growth for anode-supported cells showed a low dependence on phosphorus concentration, attributed to phosphorus activity control within the anode by bulk nickel phosphide products.

The dark clusters at the surface are composed of phosphorus as shown by the elemental map in Fig. 4. Ce appears to be absent at these clusters and it is deduced that these are nickel phosphorus compounds.



**Fig. 4: Elemental map analysis:
Yellow – Phosphorus, Green – Nickel,**

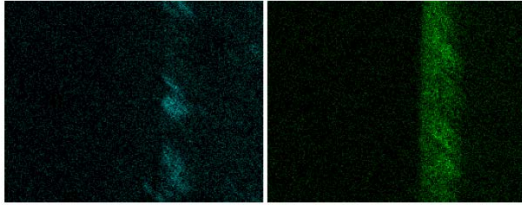


**Fig. 5: Power curves for SOFC exposed
to coal syngas containing PH3**

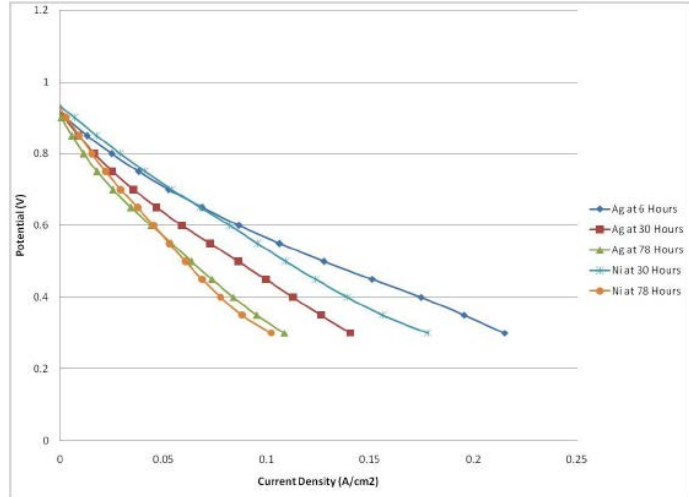
3. Effect of Silver

The objective is to determine the migration of Ag across the ScSZ electrolyte supported cell and any reaction between Ag and coal syngas. An examination on Ag migration in SOFCs was carried out to determine the reliability of SOFC testing with Ag current collecting mesh. Ag was tested as an anode and cathode current collector in SOFCs operating at high temperatures. Ag migration from the cathode current collector was tested at 900°C for 200 hours. The objective was to find if Ag migrates into the ScSZ electrolyte from the cathode to the anode. The migration mechanisms to be tested were electro- and thermomigration. Elemental mapping analysis (Fig. 6) showed Ag migrated and condensed in the LSM-GDC interlayer after the SOFC operated potentiostatically at 0.7V. However, Ag did not diffuse into the ScSZ electrolyte. Ag did not diffuse through the cathode at OCV confirming migration by electromigration. However, diffusion by thermomigration was inconclusive as the thermocouples were placed too far from the surface of the anode and cathode. The anode Ag current collector was operated at 850°C in coal syngas for 100 hours to determine if any secondary phases formed. Throughout testing, V-I scan (Fig. 7) show that Ag has smaller ohmic losses relative to the Ni current collector. This is expected because Ag has the highest conductivity of all metals. Material analysis confirms no secondary phases have formed. XRD shows only a pure Ag phase. EDXS on the Ag mesh found no nitrogen. Oxygen was only detected with silicon indicating silica from the mica seal had deposited on to the mesh. Therefore, any carbon detected on the surface is expected to be contamination and not Ag_2CO_3 . This is confirmed by thermodynamic calculations where the only spontaneous formation is Ag_2CO_3 and

Ag_2CO_3 . However, oxygen is required in this reaction but is absent in coal syngas. The anode Ag current collector does not react with coal syngas and can be safely used in short term SOFC testing.



**Fig. 6: Elemental map analysis:
Left: Silver; Right: Cerium**



**Fig. 7: V-I scans on SOFCs with Ag and Ni
current collecting mesh**

4. Effect of Trace species

Many investigations had reported the effects of major coal syngas species, such as CO and H_2 . However coal contains many trace species and the effect of these species on SOFC is rarely studied. This research focused on the effect of anticipated warm gas cleanup conditions has on trace specie partitioning between the vapor and condensed phase and the effects the trace vapor species have on the SOFC anode. Results showed that Be, Cr, K, Na, V, and Z trace species will form condensed phases and should not effect SOFC anode performance. Also the results show that Sb, As, Cd, Hg, Pb, P, and Se trace species form vapor phases and the Sb, As, and P vapor phase species show the ability to form secondary Ni phases in the SOFC anode [16].

REFERENCES

- [1]. Hepworth MT, Bender FN. (1996). *J resource management and technology*, **23**, 1–7.
- [2]. Eric G. (2009). *Energy Procedia*, **1**,4307–4334.
- [3]. Li M, Rao AD, Brouwer J, Samuelsen GS. (2010). *J Power Sources*, **195**, 5707–5718.
- [4]. Navarro RM, Pena MA, Fierro JLG. (2007). *Chem Rev*, **107**, 3952–3991.
- [5]. EG & G Technical Services, Inc. (2004). *Fuel Cell Handbook*. Morgantown, WV, US.
- [6]. Bao, J., Krishnan, G.N., Jayaweera, P., Lau, K., & Sanjurjo, A. (2009). *Journal of Power Sources*, **193**, 617-624.
- [7]. Huang, T.-J., Shen, X.-D., & Chou, C.-L. (2009). *Journal of Power Sources*, **187**, 348-355.
- [8]. Simner, S. P., Anderson, M. D., Pederson, L. R., & Stevenson, J. W. (2005). *Journal of The Electrochemical Society* , **152**, 1851-1859.
- [9]. Simner, S. P., Anderson, M. D., Coleman, J. E., & Stevenson, J. W. (2006). *Journal of Power Sources* , **161**, 115-1122.
- [10]. Nielsen, J., & Jacobsen, T. (2008). *Solid State Ionics*, **178**, 1769-1776.
- [11]. Marina, O.A., Coyle, C.A., Thomsen, E.C., Edwards, D.J., Coffey, G.W., & Pederson, L.R. (2010). *Solid State Ionics*, **181**, 430-440.
- [12]. Williams, M. C. (2007). *Fuel Cells*, **7**, 78-85.

- [13]. O'Hayre, R., Cha, S.-W., Colella, W., & Prince, F.B. (2006). *Fuel Cell Fundamentals*. New York: John Wiley & Sons.
- [14]. Salo K, Mojtahedi W. (1998). *Biomass Bioenergy*, **15**, 263–267.
- [15]. Sasaki K, Hori Y, Kikuchi R, Eguchi K, Ueno A, Takeuchi H, Aizawa M, Tsujimoto K, Tajiri H, Nishikawa H, Uchida Y (2002). *J The Electrochemical Society*, **149**, 227–233
- [16]. Tremblay JP, Gemmen RS, Bayless DJ. (2007). *J Power Sources*, **163**, 986–996.