

REVIEW ON FUEL CELL TECHNOLOGY FOR VALUABLE CHEMICALS AND ENERGY Co-GENERATION

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ABSTRACT

This paper provides a review of co-generation process in fuel cell type reactor to produce valuable chemical compounds along with electricity. The chemicals and energy co-generation processes have been shown to be a promising alternative to conventional reactors and conventional fuel cells with pure water as a byproduct. This paper reviews researches on chemicals and energy co-generation technologies of three types of promising fuel cell i.e. solid oxide fuel cell (SOFC), alkaline fuel cell (AFC), and proton exchange membrane fuel cell (PEMFC). In addition, the research studies on applications of SOFCs, AFCs, and PEMFCs with chemical production (i.e. nitric oxide, formaldehyde, sulfur oxide, C2 hydrocarbons, alcohols, syngas and hydrogen peroxide) were also given. Although, it appears that chemicals and energy co-generation processes have potential to succeed in commercial applications, the development of cheaper catalyst materials with longer stability, and understanding in thermodynamic are still challenging to improve the overall system performance and enable to use in commercial market.

KEYWORDS

fuel cells, chemical compound, industries, cogeneration

I. Introduction

1.1 Fuel cells

The production of chemicals and energy that provide high efficiency and non pollutant to environmental is a final destination for energy technologies and chemical reactors development that will soon help to sustainable development in the world. At the foreground of energy technologies, fuel cells (FCs) are expecting to find various applications in the direct convertibility of chemical reactions into electrical energy with high efficiency and small pollutant since they generate much less pollutants than combustion process.

Group of fuel cells can be divided to their electrolyte employed or working temperature (high, moderate and low temperature, etc.) For example, alkaline fuel cell (AFC), proton exchange membrane fuel cell (PEMFC), phosphoric acid fuel cell (PAFC) operates at low temperatures and aqueous electrolyte can be used. The molten carbonate fuel cell (MCFC) and solid oxide fuel cell (SOFC) operate at high temperature with molten electrolyte and solid electrolyte, respectively. Table 1 shows different types of fuel cells, distributed to the electrolyte employed, and working temperature [1]–[9].

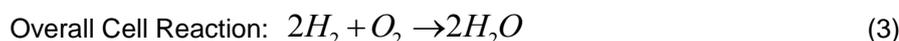
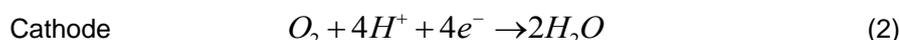
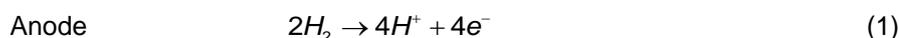
	AFC	PEMFC	PAFC	MCFC	SOFC
Temperature (°C)	60 - 90	80 - 110	160 - 200	600 - 800	800 - 1000
Electrode material	Metal or carbon	Pt-on carbon	Pt-on carbon	Ni + Cr	Ni / Y ₂ O ₃ -ZrO ₂
Electrolyte	NaOH/KOH	Polymer membrane	H ₃ PO ₄	LiCO ₃ -K ₂ CO ₃	ZrO ₂ with Y ₂ O ₃
Primary fuel	H ₂	H ₂ reformat	H ₂ reformat	H ₂ / CO reformat	H ₂ / CO / CH ₄ reformat
Oxidant	O ₂ / air	O ₂ / air	O ₂ / air	CO ₂ / O ₂ / air	O ₂ / air
Issues	CO ₂ troubles	Moisture of fuel	CO sensitivity	CO ₂ recycling necessary	Ceramic cells
Practical efficiency (%)	60	60	55	55-65 ^a	60-65 ^a

Table 1
Group of fuel cells divided to electrolyte and temperature functionalized

^a The production of additional electrical energy by means of thermal energy co-generation is not concerned [3].

1.2 Principle of Fuel Cells

A principle of FCs system composes an electrolyte solution and porous electrode e.g. anode and cathode electrode on either side. The typical fuel cell, gaseous fuels (i.e. hydrogen) are supplied continuously to the anode electrode (negative electrode) and an oxidant (i.e., oxygen from air) is fed continuously to the cathode electrode (positive electrode); the electrochemical reactions suddenly occur at the electrodes surface and produce electricity with the by-products including heat and water. The reactions are shown below.



The overall efficiency of FCs is about twice higher than internal combustion engines and other methods of electricity production from the equal amount of fuel. The

following lists summarize the most important features of FCs in comparison to other energy conversion devices [1], [3], [4]:

- FCs are power generators which are able to directly change chemical energy of fuel (hydrogen, methane, naphtha, etc.) into electrical energy which the efficiency is higher than conventional coal or gas fired thermal power stations (35-40%).
- If the waste heat of fuel cell is used in system, the fuel efficiencies are possible to go up 90%.
- Low pollution level emissions are produced from FCs (typically one to two orders of magnitude lower).
- Low noise level is generated.
- FCs require low maintenance and exchangeable parts (mass-produced components).
- The efficiency of FCs can be increased by applying the cogeneration of heat with high-temperature systems.
- For cogeneration of high temperature, waste heat is useful for many applications such as industrial processes or for additional electricity production.

1.3 Principle of Fuel Cells

As mentioned above, fuel cell is usually used as a power generator but it can be also applied as a chemical reactor. Previously, fuel cell reactors have been developed for the conversion of fuel to desired chemicals as the main product with energy generation [3] that is called chemicals and energy co-generation. In this process, the main function of fuel cell likes chemical reactor. However, electricity generated as by-product from the fuel cell reactor distinguishes it from the conventional reactor. In addition, chemicals and energy co-generation provides a benefit over a conventional fuel cell which just produces electrical and pure water as a by-product.

The typical concept of fuel cell reactor for chemicals and electrical power co-generation is illustrated in Figure 1. This system consists of fuel cell reactor, external load and chemical product recovery unit [3]. The fuel and oxidant are supplied separately to electrochemical cell (anode and cathode electrode) at fuel cell reactor, after that useful chemical and electricity are occurred. Electricity is supplied to an external load and useful chemical produced is collected. Cogeneration systems can operate at low, moderate or high temperatures; hence the electro-cogeneration process has become one of the new applications for fuel cell system.

The main advantages of the chemical and energy co-generation methods over the conventional catalytic reactors (batch reactor, plug flow reactor, continuous stirred tank reactor, etc.) are as follows [1], [3], [4]:

- The cell potential mainly controls the production in the electrochemical reactor.
- The selectivity of chemical production can be controlled by difference of the electrode potential or changing the electrode catalyst.
- The electrochemical devices can operate at very low temperatures when compare to conventional catalytic processes.
- Co-generation of electricity and useful chemical products is efficient which improve the potential of industries.
- Successful chemical cogeneration has been controlled by suitable selection of anode material and the fuel.

Therefore, fuel cell reactors for co-generation of chemicals-electrical power have become an attractive new application for fuel cell system. Many co-generation processes with different types of FCs have been discussed. Selective electrochemical oxidations of methane to synthesis gas or C2 compound with electricity in SOFC reactors are a very attractive alternative to conventional catalytic reactor. Hydrogen peroxide (H_2O_2) can be produced in an AFC reactor. PEMFC reactors show the ability to convert fuel to useful chemicals such as 1- propanol, H_2O_2 , and cyclohexamine (CHA). It is noted that this review will focus mainly on chemical and electrical power co-generation by fuel cell reactor and describes their reactions and performances.

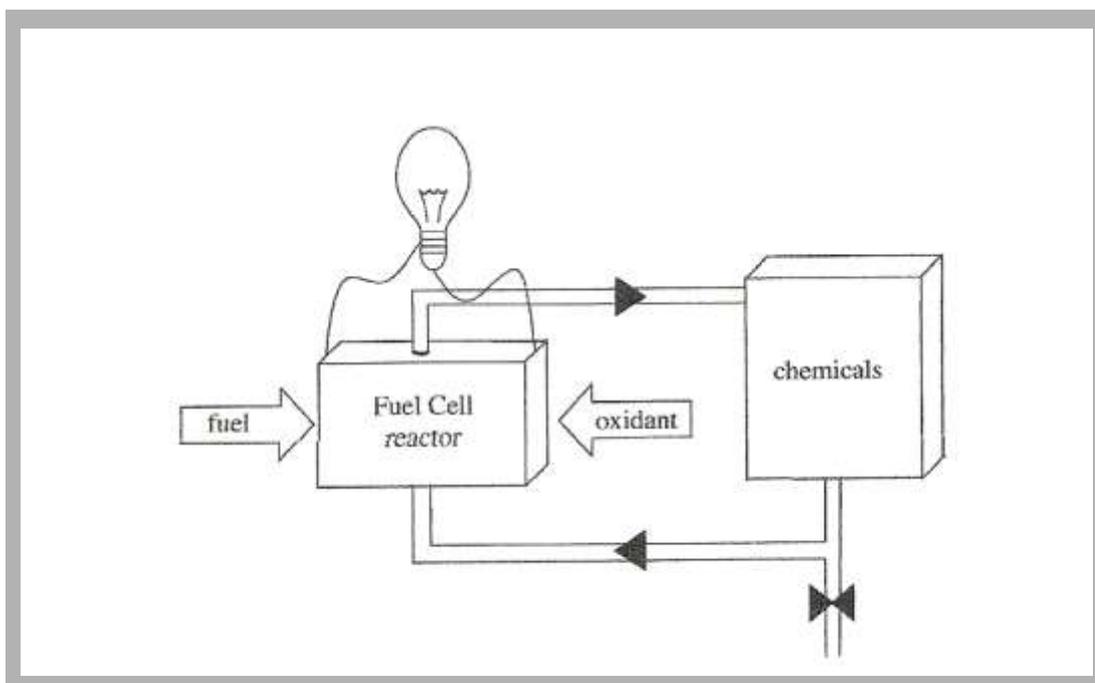


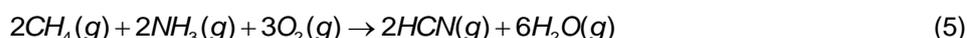
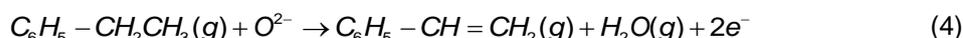
Figure 1
Principles function of fuel cell to generate chemicals and energy [3].

II. Co-generation of Fuel Cell: Chemical Production

2.1 Co-generation of SOFC Reactor

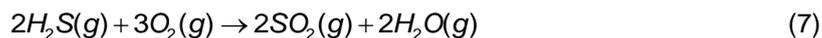
Farr and Vayenas [10] first demonstrated this type of operation for the case of NH_3 conversion to NO . They studied the nitric oxide production from oxidation reaction of ammonia and obtained electricity as by product. The result showed that, NO was obtained as a primary product with an optimal yield of over 60% when the temperature ranges from 427 to 927°C. Another interesting chemical co-generation process is the synthesis of hydrogen cyanide (HCN), which is widely used for adiponitrile (for Nylon 6/6) synthesis [11]. The selectivity of HCN exceeds 75% and approximately 0.01 W cm^{-2} of power density was obtained in the temperature range 800 to 1000 °C and 1 atm [12].

Occurring of organic compounds e.g. styrene can be studied by electrochemical oxidation of ethylbenzene dehydrogenation in SOFC. The vapor-phase electrochemical oxidative dehydrogenation of ethylbenzene on platinum-paste electrodes was studied at 575–600°C in a stabilized-zirconia electrochemical reactor. Styrene and carbon dioxide were the major products. Nevertheless, increasing in a dehydrogenation rate occur in high anodic current, total conversion was limited at only 15% or less [13].



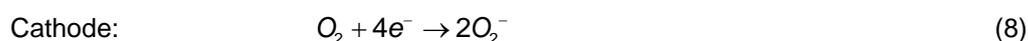
Another interesting chemical cogeneration process is the synthesis of Acrylic acid in SOFC. A highly efficient anode catalyst, $\text{MoV}_{0.3}\text{Te}_{0.17}\text{Nb}_{0.12}\text{O}$, was used for acrylic acid production from propane [14]. The partial oxidation of methanol to formaldehyde, which is an important compound for fertilizer, dyes, disinfectants, germicides and preservatives, is another important industrial reaction that has been reproduced successfully in SOFC [15]. From that work, methanol conversion was over 30%, with formaldehyde selectivity 85–92% and power density outputs obtained of about 1 mW cm^{-2} .

The oxidation reaction of H_2S to SO_2 has also been successfully demonstrated [16]. At 650–800°C and atmospheric pressure, hydrogen sulfide was oxidized on the porous Pt electrode. Hydrogen sulfide was diluted in He and used as fuel, while ambient air was used as oxidant. Reaction (6) presents the anode reaction, whereas the cathode reaction is similar to Reaction (5). Reaction (7) is the overall reaction of this system.



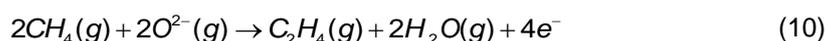
From their experiment, the selectivity to SO_2 remained under 15% is observed at low current densities ($<10 \text{ mA cm}^{-2}$) and sulfur, $(1/2) S_2(g)$, is the main product. Nevertheless, at high current densities ($>40 \text{ mA cm}^{-2}$), the SO_2 selectivity increased above 90%.

Selective oxidation of methane in SOFC was studied for co-generation of C_2 hydrocarbons or synthesis gas. As for the conversion of methane, typically, the oxidative coupling of methane has been studied mostly in conventional reactors [17] – [21]. Nevertheless, there have been few studies apply SOFC for the direct conversion of methane to useful chemicals. For instance, Solid oxide fuel cell system with membrane reactor is investigated, which anode electrode is LaAlO and cathode is LSM. When electrochemical reaction occurred, oxygen ion transferred from cathode cell to anode cell by equation (8) and (9)



In the reaction, it could produce valuable chemicals such as ethylene and carbon monoxide with high selectivity and provided electric power with high efficiency.

Pujare and Sammells [22] investigated the oxidative coupling of methane with SOFC. High C_2 hydrocarbon selectivity ($> 90\%$) was observed, although the methane conversion was relatively low. Otsuka et al. [23] also investigated similar studies over several catalysts (i.e. KF, $BaCO_3$, NaCl/ MnO_2 , Sm_2O_3) deposited on Au-electrode. The result showed that $BaCO_3$ on Au was the most active and selective catalyst. Jiang et al. [24] investigated the oxidative coupling of methane to ethylene and C_2 hydrocarbons and the yield values above 88% with 97% of the methane conversion at 800°C was observed. In their work, anodes were porous Ag film and Sm_2O porous cermet, which modified with CaO and Ag. Eqs. (10) and (11) present the anode and overall reactions of the above system.



Guo et al. [25] investigated SOFC with $Sr/La_2O_3-Bi_2O_3-Ag-YSZ$ membrane for oxidative coupling of methane and revealed that composition of membrane showed a important effect on the co-generation. The stability of membrane was continuously investigated for 62 h and no activity obviously declined (C_2 -selectivity and CH_4 conversion showed relatively stable). Kiatkittipong et al. [2], [26] investigated solid oxide fuel cell reactor using $La_{0.85}Sr_{0.15}MnO_3/8 \text{ mol}\%Y_2O_3-ZrO_2/La_{1.8}Al_{0.2}O_3$ for C_2 hydrocarbon production. A schematic of SOFC reactor for C_2 hydrocarbon production is shown in Figure 2. The most of C_2 production is ethylene, which is more favored than ethane. However, the influence of increasing methane flow rate effected to the decreasing methane conversion while C_2 selectivity slightly increases.

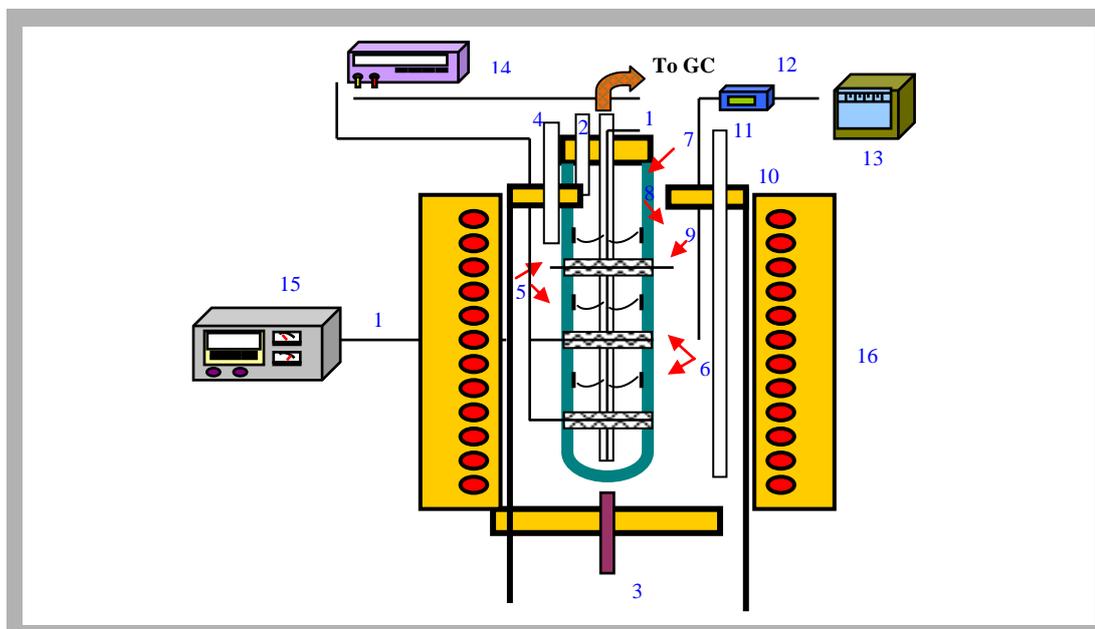


Figure 2
Experimental setup of laboratory for SOFC to C2 production [2].

- | | |
|--|--|
| 1. Anode side feed (CH ₄) | 2. Exit gas from anode side |
| 3. Cathode side feed (O ₂) | 4. Exit gas from cathode side |
| 5. Pt wire | 6. Platinum mesh |
| 7. YSZ tube | 8. Anode (Au/ La _{1-x} Sr _x MnO ₃) |
| 9. Cathode (La _{1-x} Sr _x MnO ₃) | 10. Quartz tube |
| 11. Thermocouple | 12. Temperature indicator |
| 13. Temperature recorder | 14. Ammeter/Voltmeter/Potentiostat |
| 15. Temperature controller | 16. Furnace |

Syngas and electrical power in direct-methane solid oxide fuel cell (SOFC) was reported [27] – [33]. Syngas can be used as feedstock for hydrocarbon and methanol manufacture. The syngas co-generation enhanced when increasing bulk lattice-oxygen extraction from electrochemical reaction [31] – [37]. This observation occurred when providing external potential to the electrochemical cell, ionic species migrated to the electrode surface and makes the changing the operation of catalysts electrode, which corresponded to a change in activation energy and the rate of catalytic reaction. This observation can be applied to supply methane in a period for the synthesis gas and electricity production, in which electrical current is obtained when fed methane just one fifth of overall working time [36].

Ishihara et al. [38] studied the co-producing of syngas and electricity by SOFC. Partial oxidation of methane $CH_4 + 1/2O_2 = CO + 2H_2$ as internal reforming reaction was investigated. From their study, the maximum power density of 526 mW cm⁻² with synthesis gas yield of 20% can be achieved. Similar investigation was performed by Pillai et al. [39]. They reported that, SOFC produced 0.9 Wcm⁻² and methane was converted to syngas with 90 % of methane conversion at a rate of 30 sccm cm⁻², 750 °C.

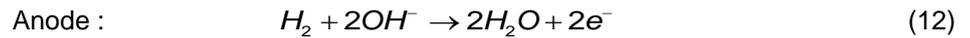
The possibility of synthesis gas and electricity production from electrochemical partial oxidation of CH₄ in SOFC has been studied by numerical simulation. In catalytic reaction of CH₄, energy occurring in the partial oxidation reaction at perovskite cathodic electrode can be supplied in flow reversal operation in SOFC. Thermodynamic efficiency occurred in the reaction showed exceeding unity ($\eta > 2$), which revealed the interesting in the SOFCs to produce valuable chemicals and electrical energy [40].

According to economic analysis of SOFC for chemical cogeneration, until now, very limited works have been reported. Brousas et al. [41] designed SOFC plant for complete oxidation of methane to CO₂ and H₂O while another SOFC plant was aimed for synthesis gas and electricity. They evaluated these systems and were found that the synthesis gas was low. Therefore, SOFC plant coproducing synthesis gas has so far to expand to large-scale application. Vayenas et al. [42] proposed the index for evaluating the relative profitability of SOFC chemical co-generation compared to the chemical reactor at same product capacity and composition. Only SOFC reactor using inexpensive material with exothermic reaction might be beneficial. The results showed

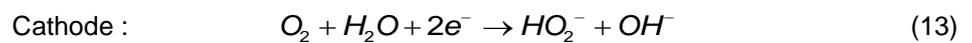
that H_2SO_4 and HNO_3 cogeneration were possibly advantageous while ethylene oxide and formaldehyde production were not.

2.2 Co-generation of AFC Reactor

Several authors [3], [5], [43]–[46] have described that AFC enables to produce hydrogen peroxide and electricity. These cathode electrodes are usually made from carbon cloth covered with a layer composed of catalyst mixed with carbon black and low proportion of PTFE (Polytetrafluoro ethylene) whereas a carbon cloth covered with a Pt-catalyzed C-PTFE layer are anode electrodes surface. Thus, Alcaide et al. [43] have proposed HO_2^- production from undivided alkaline fuel cell, which consists of anode, cathode and KOH electrolyte. This experiment has been studied with small electrode, and operated in batch or continuous system. At the anode; H_2 gas occurred oxidation and obtain water from the following two-electron reaction:



Cathode, O_2 gas occurred reduction to HO_2^- by following two-electron process.



The overall reaction in the AFC can be written as follows:



When KOH recirculation solution is used, the performance of AFC was down. When fresh KOH solution was continuously added, the current densities was 100 mA cm^{-2} and current efficiency closed 100% with 1.0 mol dm^{-3} KOH at 20°C .

Brillas et al. [44] built up a small-scale undivided flow AFC provided electrical energy and HO_2^- . Fresh KOH solution has been chosen as electrolyte and was circulated through AFC. For AFC system, a carbon cloth without catalysed C-PTFE layer was cathode electrode while anode electrode modified with Pt-catalysed C-PTFE layer. At external load (R_{ext}) = 0.10Ω , the current efficiency reached 100% and the current density of more than 100 mA cm^{-2} are obtained over KOH concentrations at 1.0 M at 45°C and for higher KOH concentrations at 25°C and electrolyte flow of 20 ml min^{-1} . Figure 3 shows AFC fuel cell reactor system. Alcaide et al. [45] studied O_2 diffusion cathode and H_2 -diffusion anode in a flow alkaline fuel cell for hydrogen peroxide generation. The porous E-TEK carbon cloth electrode was anode, which modified with 10% Pt on Vulcan XC-72 carbon black (0.5 mg cm^{-2} Pt loading) and O_2 -diffusion cathode was E-TEK. The experiment show that combination flow alkaline fuel cell with hydroperoxide ion production was limited. The reason due to carbon of the H_2 -diffusion anode did not react with oxygen during occurring hydroperoxide ion production in the AFC.

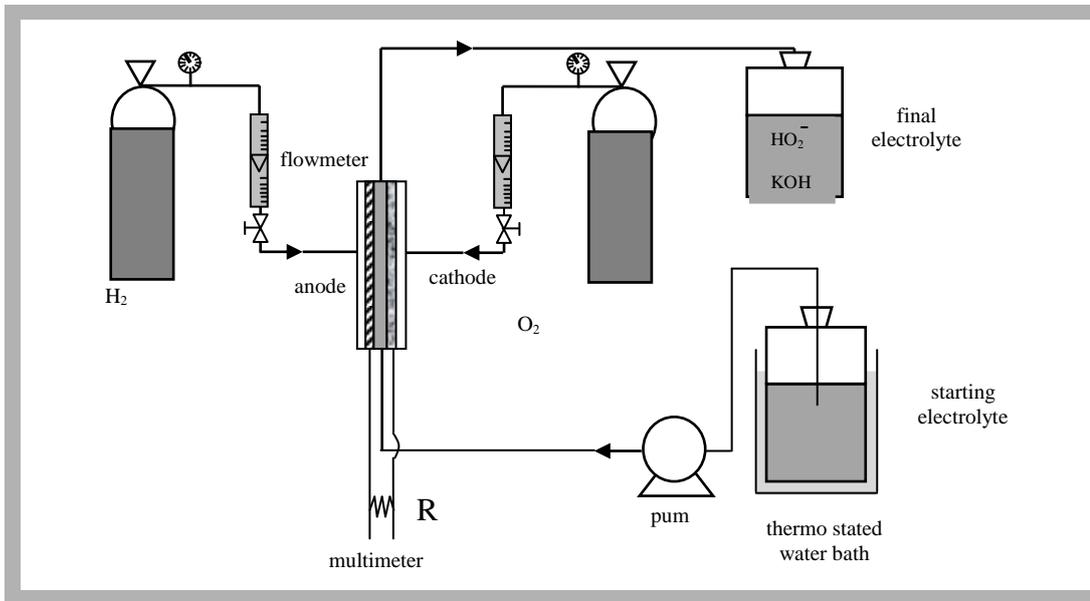


Figure 3
Experimental setup of
AFC [44]

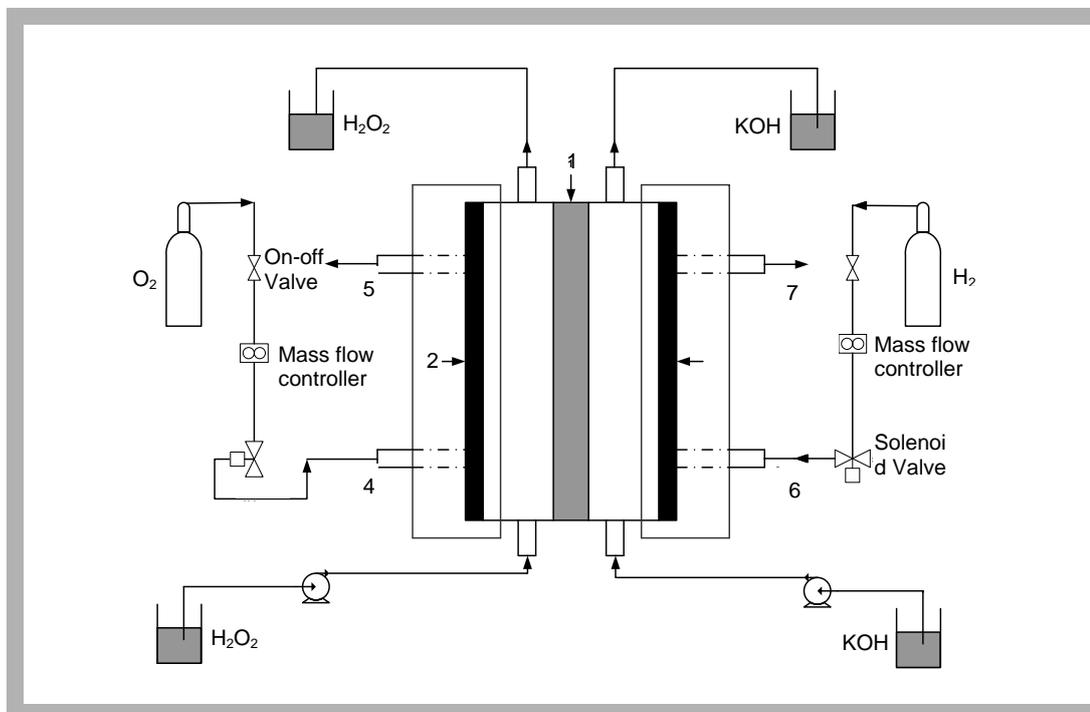
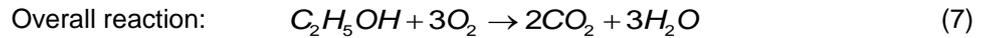


Figure 4
Scheme of AFC [46]

- | | |
|----------------------|---------------------|
| 1 Nafion Electrolyte | 2 Cathode Electrode |
| 3 Anode Electrode | 4 Oxygen entrance |
| 5 Oxygen exit | 6 Hydrogen entrance |
| 7 Hydrogen exit | |

Fuyuan et al. [46] reported H_2O_2 production through AFC using CeO_2/MWNT (multi-walled carbon nanotube) as the O_2 -diffusion cathode electrode and 40%Pt/C was the catalyst for modification H_2 -diffusion anode electrode. The purity of H_2 at 0.1 MPa was fed to anode, whereas O_2 of 100% was flowed to the cathode at 0.1 MPa. KOH electrolyte was continuously fed to anode chamber while distilled water was added to cathode chamber. Figure 4 shows the schematic view of AFC fuel cell reactor system. The results indicated that hydrogen peroxide production of 275 mmol/L was success at 25% of CeO_2/MWNT , 18 ml/h of aqueous solution, and 5 mol/L of KOH electrolyte in AFC. The results also revealed that MWNT and cerium oxide were suitable catalyst material to produce hydrogen peroxide.

In addition, alkaline direct ethanol fuel (ADEFC) is also constructed to provide energy for small-scale applications e.g. portable electronic equipment [47-49]. Actually, ethanol is selected to fuel in AEFC owing to non-toxic chemical. Ethanol occurred with deep oxidation to carbon dioxide which involved a 12-electron process:



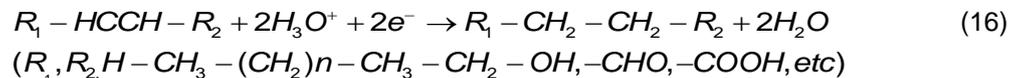
The performance of ethanol oxidation in alkaline solution was higher than acid solution due to less positioning of intermediate from ethanol oxidation at Pt anode electrode. For this reason, non-Pt electrode and Pt alloy catalyst can be used in ADEFC. Modestov et al. [49] reported the fabrication of membranes of phosphoric acid for ADEFC and apply to emergency power supply units. A membrane of phosphoric acid was constructed with non-platinum electrocatalysts and a membrane of alkali doped polybenzimidazole (PBI). It was found that the dropping KOH to PBI lead to increase ionic conductivity. According to the report in that work, the single cell runs with 3 M KOH + 2 M EtOH anode feed and can provide power density of 100 mW cm^{-2} , $E = 0.4$ at 80°C using air at 0.1MPa.

2.3 Co-generation of PEMFC Reactor

Actually, conventional electrochemical hydrogenation has been reported on an electrolysis cell. Humidified H_2 gas is supplied to the anode and hydrogen occurred oxidation reaction according to Eq. (15):

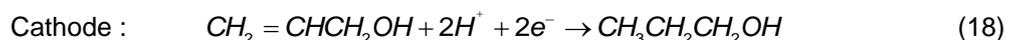


After that, protons migrated to the ion-exchange membrane and electrons suddenly passed through the external circuit. At cathode cell, H_3O^+ ions reacted with unsaturated compound (electrochemical hydrogenation) as shown in Eq. (16)



Many unsaturated organic alcohols such as allyl alcohol, propargyl alcohol, 2-buten-1,4-diol, 2-buten-1,4-diol and acids (maleic acid, acrylic acid, crotonic acid, acetylenedicarboxylic acid) are oxidant substances which combined with hydrogen fuel in PEMFC. Electrochemical cell in a PEMFC consisted of gas diffusion electrodes (GDEs) which composed 20% Pt/C on Vulcan XC-72 (obtained from De Nora-ETEK). Pt of $0.35\text{--}0.50 \text{ mg cm}^{-2}$ was loaded for the anode, loading 4 mg cm^{-2} of Pt for the cathode, and Nafion was electrolyte. The useful hydrogenated products and electric energy in PEMFC is apparent. The formation of allyl alcohol, 2-butene-1,4-diol and acrylic acid was obtained, which current densities has been achieved more than 50 mA cm^{-2} and maximum power densities was approximately 1 mW cm^{-2} . [50].

The hydrogenation of allyl alcohol (AA) to 1-propanol was also described in PEMFC with a membrane electrode assembly (MEA) [51]. Anode and cathode were 20% Pt/C catalyst [51]. Figure 5 shows the experimental schematic view of PEMFC reactor system. According to the result, 1-propanol was only product and 100% selectivity to 1-propanol was obtained without side reaction occurring. The reactions are as follows:



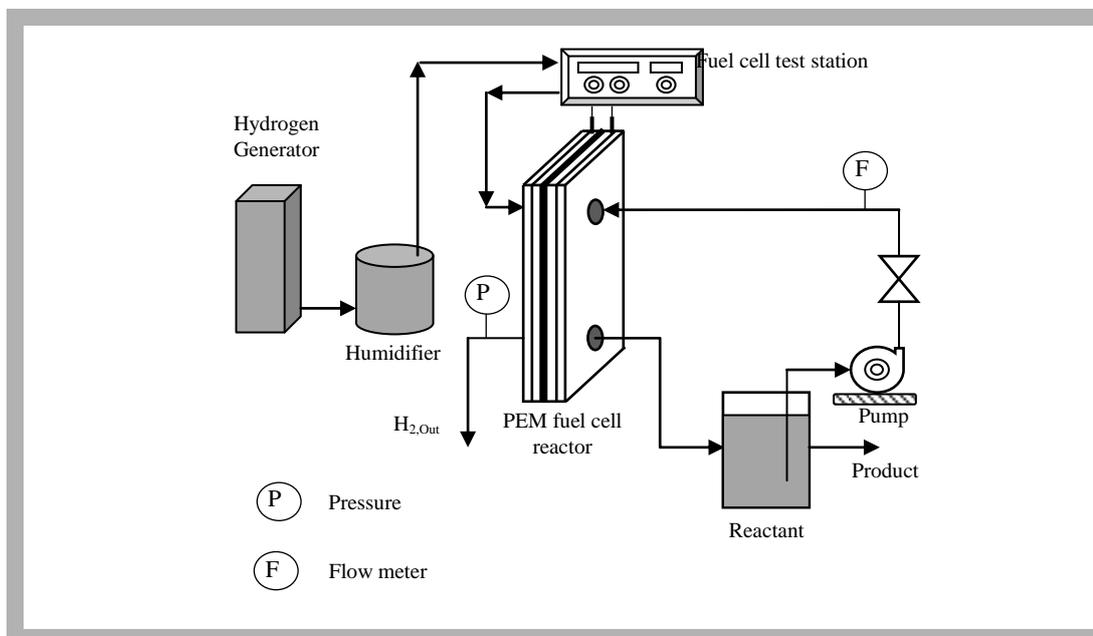
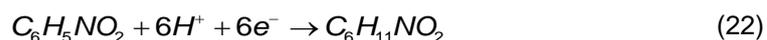
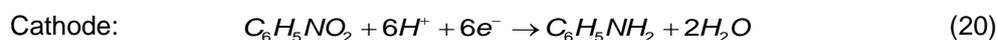


Figure 5
A schematic view of PEM fuel cell reactor system [51].

Another interesting chemical cogeneration process is the synthesis of cyclohexylamine (CHA), which is widely utilized as protective film former to resist the metal corrosion from oxidation reaction, and was added in paper- and metal-coating industries to help resistance moisture [52],[53]. In addition, CHA can help human from syncytiotrophoblast [54]. CHA is also utilized as a polyamide polymerization chain terminator that controls polymer molecular weight [55]-[57]. Many researches showed that co-generation of CHA and electrical energy can be obtained in a PEMFC which was selective with reduction of nitrobenzene (NB) [58]. In PEMFC experiment, hydrogen flow rate was supplied with 20 ml min^{-1} at $70 \text{ }^\circ\text{C}$ for 2 h. and CHA selectivity of 57.3%, 28.2% for aniline (AN), with 8.2% conversion of NB were received. These equations of each reaction on anode and cathode are as follows:

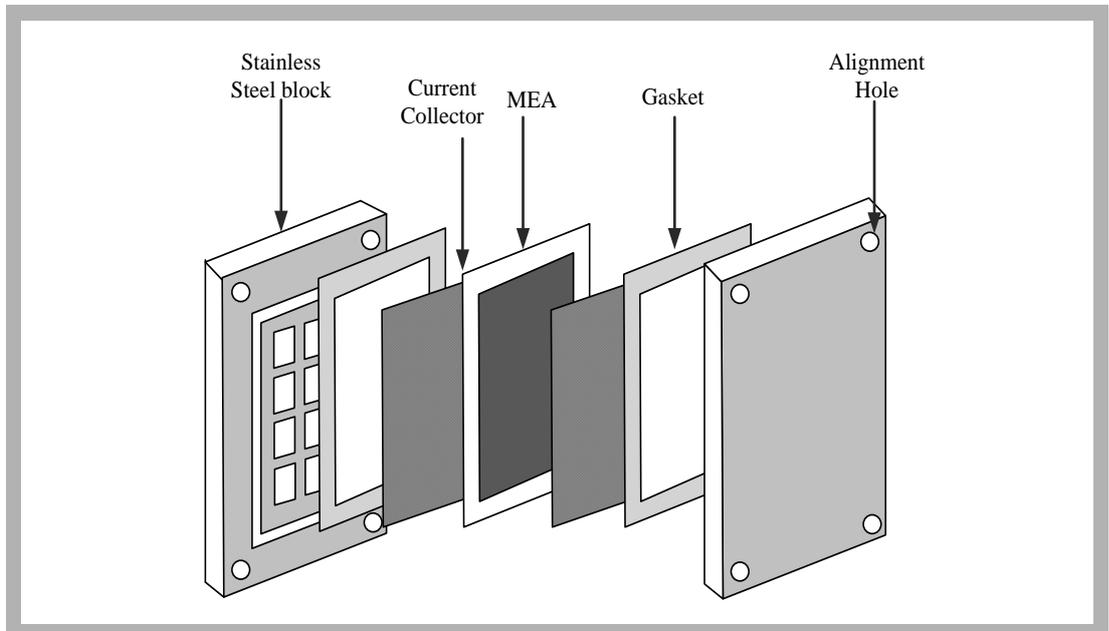


For the reactions (20) and (21), products are valuable. However, a by-product, nitrocyclohexane (NCH), may be formed via side reaction (22).

One step synthesis of phenol has been studied with much more attention [59,60]. Industrially, phenol is a useful chemical which was used for an intermediate in the synthesis of several petrochemicals. The fuel cell system, [O_2 , Benzene, FeCl_3 (FeSO_4 , CuCl_2 , CuSO_4 or SnCl_2) in HCl or H_2SO_4 aq., Pd (or Au)/Nafion-H/Pt, H_2], produced phenol selectively and continuously generated electricity power. These systems reduced Fe^{III} to Fe^{II} or Cu^{II} to Cu^{I} and obtained H_2O_2 .

Co-generation of phenol production in proton exchange membrane fuel cell (PEMFC) has been studied by Cai et al. [60]. The PEMFC reactor was shown in Figure. 6.

Figure 6
Scheme of PEMFC
reactor [60].

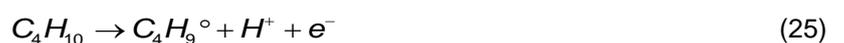


The in situ PEMFC reactor could generate peroxide, which reacted with benzene and received phenol chemical. From their experiment was showed that rate of phenol formation was controlled by changing current or potential.

H_2O_2 has many advantages such as pulp bleaching process, and waste treatment. The fuel cell system [O_2 , HCl aq. or H_2SO_4 aq., M (cathode)/Nafion—H/Pt(anode), H_2] where M is Pt, Pd, Au, graphite or Au-mesh, cogenerates H_2O_2 and electricity [61]. At the early stage of the reaction, the current efficiency for the formation of H_2O_2 was 100%. However, the efficiency sharply dropping from 100% to 70% during 3 h due to the electrochemical reduction of H_2O_2 to water and/or thermal decomposition of the H_2O_2 at cathode electrode - the result is similar to previous report of Yamanaka et al. [62].

In addition, the catalysts stability is also an important parameter to study due to effect to H_2O_2 formation. H_2O_2 formation rates in PEMFC for Pt, Pt binary (PtX, X = Co, Ru, Rh, V, Ni) and ternary (PtCoX, X = Ir, Rh) catalysts modified on ketjen black (KB) carbon were investigated [63]. Single-sided membrane electrode assembly (MEA) with a built-in reference electrode was employed to study the rate of H_2O_2 formation and stability of PtCo and PtIrCo on Nafion membrane in PEMFC. The degradation of membrane was displayed by fluoride ion concentration in the effluent water. The comparison of stability was found PtIrCo < PtCo/KB < Pt/KB. The selectivity for H_2O_2 formation showed that PtCo and PtIrCo was higher selectivity than unalloyed Pt, membrane degradation did not observed on these catalysts.

Hydrocarbons fuels such as ethane, propane and butane have been used in PEMFC, and are oxidized to hydrocarbon more than six carbons [64]. The propane, butane and ethane fuels were supplied to the anode. In PEMFC system, 20% carbon-loaded Pt as catalyst was anode and cathode electrodes and also used Nafion membrane. From that experiment, increasing the maximum power output was involved to treat Nafion membrane with phosphoric acid. For example, fuel cell with unmodified membrane with phosphoric acid was $0.0182 \text{ mW cm}^{-2}$ of the maximum power output but was 0.143 mW cm^{-2} for the cell with modified membrane. For reaction oxidation in PEMFC, ethane occurred oxidation reaction at anode electrode and obtained hexane and octane as products. Therefore, ethane oxidation at the anode of ethane/oxygen fuel cell may involve:





Ethane occurred oxidation reaction to produce hydrocarbon products such as Hexane and octane. The results that hexane product was occurred by propane oxidation reaction while obtained octane from occurring butane oxidation.

A lot of works have been focused on running on natural gas to hydrogen production [65], [66]. Recently, Radulescu et al. [65] reported an experimental and theoretical results of a study of five identical CHP units (Cogeneration Heat and Power) using PEMFC to produce hydrogen from natural gas reforming. The accuracy of the results of simulation was satisfied and can forecast the performance of PEMFC system. Doucet et al. [66] studied the H₂ separation from hydrogen/ethylene mixture using PEMFC and separation of hydrogen and hydrogen process has been explained by mathematical pattern; the model showed similar result to PEMFC experiment.

III. Prospect

Aside from start to an efficient power electricity generator, that fuel cell reactors really show another a very interesting application to produce valuable chemical as the main products together with the current delivered at the same time, which this process is called electro-chemical co-generation. There are many electro co-generation processes in different typed of FCs, that provide various products. Thus, electro co-generation has a major driven development towards commercialization. Overall, most industries should satisfy and should be able to apply the electro co-generation in their own processes due to it show possibility for controlling the selectivity of product and % conversion with adequate current efficiency.

However, in fuel cell reactors, two main technical apertures have been indentified: high price and low stability. The catalysts material in fuel cell is the major obstacle to these applications. Up-to-date, although plenty of efforts in fuel cell catalysts have been focused on price-reasonable of synthesis, active, and high stability, no true breakthrough has been reported yet. Thus, find out progress catalysts; increasing catalysts activity (e.g., particle size, conductivity, dispersed of catalysts on the support), and stability (etc. tolerance to CO₂, CO, SO₂); and reduced cost of catalyst are the important mission and challenge in fuel cell reactors for opening the opportunity in commercialization. In addition, the understanding in the reactions of fuel cell reactor including thermodynamic (e.g., entrophy, cooling effect, hot spot) is required to develop the optimal condition for enhancing fuel cell activity.

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