Potentials of the direct use of ethanol fuel cell as backup electricity for renewable energy system

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Abstract

The issue of renewable energy has received considerable critical attention. This has led to a decline in the population of Greenhouse Gas (henceforth GHG) emissions, health-risk related emissions and energy security. The main challenge faced by many researchers is major issues of low reliability for producing electricity from solar PV. Wind energy has accentuated the problem of sharing of these renewable energies down in the National Energy plans. The solar PV and wind energy may cause fluctuation depending on the daytime and season. The backup electricity is required for increasing reliability of these renewable energy sources. It is now well established that the Direct Ethanol Fuel Cell (henceforth DEFC) is a high bio-fuel production country. Ethanol also has many advantages such as, high energy density, easy for storage and transport, less dangerous to handle compared to hydrogen gas. In addition, the energy efficiency of DEFC is comparable to that of other fuel cell technology. The low operating temperature means less startup period and thermal input energy. This study aims to analyze the potentials to use DEFC as backup electricity for the renewable energy system. The performance characteristics were examined according to updated experimental results. The advantages and challenges were also discussed in this study.

Keywords: Reliability, Backup electricity, Ethanol, Renewable.
1. Introduction

Depending on global economic development and growth of energy resource demand, the GHG emissions are inevitably produced leading to worldwide climate change crises, e.g., increasing average ambient temperature, fluctuating ultimate rainfall-amount, extreme and unpredictable weather condition. The change in average global temperature may accelerate genetic changing [1] and contribute to newly emerging diseases [2], including the ongoing global pandemic of corona virus disease 2019 so-called COVID-19. One of the greatest challenges for Thailand economy is rapid development that may lead to GHG emission production and with high fossil energy dependence. The trends of economic activity development (GDP and population) and GHG emission are shown in Figure 1(a), resulting from various economic sectors and primary energy consumption (see Figure 1(b) and Figure 1(c)) [3].

Electricity produced from industrial activities and transport sectors is the leading cause of the highest GHG emission. The energy consumption is insecurely dominated by fossil energy, more than 80% depending on natural gas and crude oil. It is now well established that the economic activity can impair global pandemic of corona virus disease 2019.

To mitigate GHG emission and improve energy security, renewable energy is supported in Thailand through the Alternative Energy and Development Plan (AEDP [4,5]). Beside of biodiesel and ethanol for suppressing transport fuels and other primary energies for heat generation, the natural energy sources, such as hydropower, biomass, photovoltaics and wind turbines, are widely regarded for electricity. However, some kinds of these renewable sources are defined as the variable renewable energy (henceforth VRE) [6] because those are non-dispatchable due to its fluctuating and low reliable nature, such as wind power and solar power. The hydropower also relies on seasonal rainfall while the biomass, which is generally a byproduct of the agricultural sector, depends on the overall planting season. Expanding the share of these renewable energies requires essential supply-demand management.
and induces interesting on energy storage technology [7]. The energy storage system absorbs energy and stores it for some time, before releasing supply energy when renewable power down. The energy storage technology is the necessary components in the most energy system, especially the VRE to achieve a low carbon future. However, there are some disadvantages and limitations in applying energy storage technology especially the investment cost and short-life time. Therefore, the backup generator is required to optimize investment cost depending on the size of backup electricity. The fuel cell technology is another alternative environmental-friendly option of backup electricity generation in coupling with the VRE or other renewable energy. Supplied fuels can be the carbon-free hydrogen or the carbon-neutral ethanol from a cultivated plant. In a reason that the ethanol supplied-chain has already completed in Thailand [8]. It can be produced from agricultural products such as molasses, sugarcane juice and cassava. Comparing to methanol, ethanol has a greater advantage in mass-energy density and less toxic. Moreover, it is easy for storage and distribution compared to hydrogen fuel. Therefore, the Direct Ethanol Fuel Cell (DEFC) is focused in this study. The main objective is to highlight potentials to use DEFC for backup electricity application and describe challenge issues.

2. Direct ethanol fuel cell reviews
The direct ethanol fuel cell (DEFC) is an electrolyte class of the lowest operating temperature, ranging from low to high order of 1) polymer electrolyte or proton-exchange membrane fuel cell (PEFC or PEMFC), 2) alkaline fuel cell (AFC), 3) phosphoric acid fuel cell (PAFC), 4) molten carbonate fuel cell (MCFC), and 5) solid oxide fuel cell (SOFC). Some details of each fuel cell categorize are shown in Table 1 [9].

| Electrolyte | PEFC (PEMFC) | AFC | PAFC | MCFC | SOFC |
|-------------|---------------|-----|------|------|------|
| Electrodes  | Hydrated polymeric ion exchange membranes | Mobilized or immobilized potassium hydroxide in asbestos matrix | Immobilized liquid phosphoric acid in SiC | Immobilized liquid molten carbonate in LiAlO₂ | Perovskites (Ceramics) |
| Catalyst    | Platinum      | Platinum | Platinum | Electrode materials | Electrode materials |
| Interconnect| Carbon or metal | Metal | Graphite | Stainless steel or Nickel | Nickel, ceramic or steel |
| Operating temperature | 40 – 80 °C | 65 – 220 °C | 205 °C | 650 °C | 600 – 1000 °C |
| Prime cell components | H⁺ | OH⁻ | H⁺ | CO₃⁻ | O²⁻ |
| Product water management | Evaporative | Evaporative | Evaporative | Gaseous Product | Gaseous Product |

As can be seen from Table 1 above, we consider using alcohol as one of the energy sources of the fuel cell. The alcohol solution can be directly fed into the anode side while oxygen or air is fed in another cathode side (see also Table 2) [10]. At the Anode side, the active fuel solution breaks down and provides active protons diffused through the separated electrolyte layer. The active electrons flow through the electric junction and release the electricity. At another Cathode side, the oxidant receives inactive
protons and the electrons form water as the fuel cell products. The performance of this alcohol fuel cell can be maintained by compromised proton diffusing rate with the alcohol crossing over characteristics.

**Table 2.** The stoichiometric chemical reaction in PEMFC and schematic diagram

|                                | Anode                   | Cathode                              |
|--------------------------------|-------------------------|--------------------------------------|
| **PEMFC** H₂ and oxygen/air    | 2H₂ → 4H⁺ + 4e⁻         | O₂ + 4H⁺ + 4e⁻ → 2H₂O                |
| **DMFC** methanol and          | CH₃OH + H₂ → CO₂ + 6H⁺ + 6e⁻ | 3/2 O₂ + 6H⁺ + 6e⁻ → 3H₂O            |
| oxygen/air                     |                         |                                      |
| **DEFC** ethanol and oxygen/air| C₂H₅OH + 3H₂O → 2CO₂ + 12H⁺ + 12e⁻ | 3O₂ + 12H⁺ + 12e⁻ → 6H₂O            |

**Figure 2.** Electricity storage applications and technologies [15]

For the direct alcohol fuel cell, the DEFC uses ethanol feeding to fuel cell instead of the more toxic methanol as the Direct Methanol Fuel Cell (DMFC). Ethanol is a more promising option in Thailand than methanol because it comes with a supply chain that is already in place. Ethanol is a hydrogen-rich liquid and it has a higher specific energy (8.0 kW/kg) compared to methanol (6.1 kWh/kg) or better energy density (6.28 kWh/liter) compared to compressed hydrogen (0.18 kWh/liter, for 70 bar 25°C
hydrogen). Ethanol can be obtained in great quantity through a fermentation process of renewable energy resources such as molasses, sugarcane juice and cassava produced in Thailand or from wheat, corn and straw. Bio-generated ethanol (or bio-ethanol) is thus attractive since growing crops for bio-fuel production absorbs much of carbon dioxide emitted into the atmosphere by burning the bio-fuels themselves, as the carbon-neutral fuel. This is in sharp contrast to the use of fossil fuels. Ethanol also remains the easiest fuel to work with and is important for a wide range of use to the consumers. There is evidence that ethanol plays a crucial role in regulating the storage and infrastructure challenges of hydrogen for fuel cell application. To use DEFC as backup electricity for the renewable energy system, ethanol can be stored in a long time without additional cost. Otherwise, it can provide continuous electricity as long as fuel is providing. Figure 2 [11] shows the electricity providing duration (similar to battery discharge duration) from various backup electricity (or electricity storage) applications and technologies.

The hydrogen and fuel cell can provide long electric supply in a wide range of output duration rather than other technologies. Likewise, the DEFC, which is a PEMFC type, has the lowest operating temperature (see also Table 1). It theoretically requires the shortest start-up period [12, 13, 14], among other fuel cell system as well as shorter than internal combustion engines. For prolong discharge duration, the battery energy storage needs additional battery capacity, so investment cost increases. However, the hydrogen and fuel cell can continuously supply electricity as long as the fuel is fed. Figure 3 [15] presents the relationship of investment cost risen and discharge duration for various backup electricity technologies. The DEFC and other fuel cell system provide a reduction of investment cost to prolong discharge duration than the others.

![Figure 3. Energy storage cost risen as a function of discharge duration [11]](image)

### 3. DEFC performance study

This section presents progress of DEFC performance study followed the experimental investigation and theoretical calculation in the previous works [14, 16, 17]. By using a micro-DEFC demonstration kit (4.0 cm² active area, 100/1,400/177.8 µm of Catalyst/Diffusion/Membrane layer thickness [18]), electrical performances were measured by varying ethanol quantity (95% purity) in 60 mL Anode-side active liquid mixture (blending with water) coupled to the atmospheric air Cathode side.
The details on the Figure 4 are: 1. Lid set (Micro-DEFC), 2. Vane set, 3. Membrane (MEA), 4. Set structure (Micro-DEFC) and 5. Cylinder solution. Bio-energy feed ethanol set is fuel direct demonstration for changing the ethanol fuel to electrical energy.

A small heater with temperature controller was dipped in active ethanol-water mixture tank so the operating temperature can be maintained. The output electric junctions were attached to a small fan as an electric load, so the cell performance can be observed. The operating parameters were measured using a high-speed data acquisition from National Instrument. Table 3 provides the calculated ethanol concentration according to the ethanol quantity in the mixture. The temperature of micro-DEFC demonstration kit was varied between 30 – 65°C.

### Table 3. Ethanol quantity in 60 mL Anode-side active liquid mixture [14, 16, 17]

| 95% ethanol quantity (mL) | Ethanol concentration (%) |
|--------------------------|---------------------------|
| 5                        | 7.92%                     |
| 7                        | 11.08%                    |
| 9                        | 14.25%                    |
| 11                       | 17.42%                    |
| 13                       | 20.58%                    |
| 15                       | 23.75%                    |

The results of DEFC performance (Current density, Power density and Cell Voltage) in various conditions are shown in Figure 5. It was found that the performance of the demonstration DEFC kit increases with operating temperature as cell voltage, current density and power density increasing. However, the cell performance tends to fall with ethanol concentration achieving some condition. On the other hand, the optimum operation can be obtained at the cell temperature of 51°C. The current density, power density and cell voltage increase continuously with ethanol concentration at this operating temperature. The current density can be varied between 3.35 – 4.83 mA/cm² and the power density can be varied between 3.19 – 4.76 mW/cm², at a nearly constant cell voltage of 0.97±0.01 V. The maximum power of this DEFC is 76 mW according to 2 cm × 2 cm of cell active area at the maximum ethanol concentration of 23.75 %vol.
4. Advantages and challenged issues of the DEFC
The performance characteristics of the DEFC were observed in this study. The alcohol crossover the cell is a specific characteristic of the direct alcohol fuel cell. The alcohol crossover rate is generally increasing with temperature, current density, and feed concentration [12, 16, 17, 19, 20]. These characteristics have a more influence in the DMFC (Direct Methanol Fuel Cell) type. However, this alcohol crossover can be minimized within the operating temperature range. This current study revealed that the cell performance fell with ethanol concentration for mostly operating temperature conditions, excepted at the observed optimum temperature of 51°C where the crossover can be maintained and the ethanol concentration can be further increased (see in Figure 5). Therefore, the advantages and challenging issues of the DEFC can be discussed below.

4.1 Reviewed of key advantages of DEFC
- **More sustainable energy source**: The DEFC uses ethanol as the energy input, which is the better attractive than other fuels. Ethanol can be obtained from sustain-renewable resources such as molasses, sugarcane juice and cassava produced in Thailand or from wheat, corn and straw. This gives the ethanol in sharp contrast to fossil fuel since growing crops for biofuel production absorbs much of carbon dioxide emitted into the atmosphere. It has higher energy content compared to hydrogen and methanol, which also has higher toxicity. The infrastructure and storage of ethanol ease to be maintained compared to hydrogen. Besides, the ethanol can be stored in a long time without additional cost and can provide
continuous electricity as long as fuel is providing. This gives much more attractive than the battery energy storage to prolong continuous electricity supply.

- **Low operating temperature and less start-up period**: Low optimal operating temperature has been confirmed from the observed results (51°C), as shown in Table 1. Therefore, the DEF (and all PEFC) requires the shortest theoretical start-up period compared to other fuel cell technologies, as well as shorter than internal combustion engines.

- **Other advantages**: Comparing to the electric generator with internal combustion engines, the DEF has better thermal efficiency in both theoretical and practical viewpoints. The current retail-fuel station is applicable for ethanol supply. The vehicle technology shifts toward electric vehicles will give more opportunity on DEF because there will be excessive ethanol production from available ethanol supply-chain.

### 4.2 Challenged issues reported in the literature

- **DEF up-scaling**: The major weakness of DEF is that there is currently not any successive large-scale DEF power production, for both cells up-sizing or prototype stack such as a 100 kW power production. The current DEF are only micro-FCs. The available 10 kW DEF [21] which success in laboratory prototype composes of ten 36 cell-stacks (27.7 W each with 18 cm × 18 cm active area). The major up-scaling issue depends on several weakness such as in-complete reaction of feed ethanol, low ethanol concentration in practical operation, a difficulty of carbon-carbon bond breaking [20].

- **High cost of catalyst materials**: Like many fuel cells types, the major drawback of DEF is the cost related to catalysts. However, the cost related issue may become minor due to demand development with renewable power plant expansion. Furthermore, one research direction considers the Anion-Exchange Membrane (AEM), which involve on hydroxide ion conduction in electrolyte instead of the proton. The AEM concept allows the possibility to use non-platinum, less expensive, metal catalysts.

- **Matching with electricity load requirement**: Like other fuel cell or any electric generation technology, the supplied electricity must balance with load demand. The over voltage or power shortage issues will cause widely-damage for many electric devices, reduce technology confidence and slow down the production volume to achieve mass-production levels. This issue requires more effort on research and development.

### 5. Conclusion

This study has shown that the Direct Ethanol Fuel Cell (DEF) is considered as another option of backup fuel cell generator for Variable Renewable Energy (VRE). It is selected instead of other active fuel cell reactant (e.g., hydrogen, methanol, natural gas) because the ethanol is one of the most sustainable energy in Thailand. This study has found that generally, the DEF is one fuel cell technology which operates in the lowest operating temperature so it requires shorter start-up period so appropriates in backup generator application. The experimental investigation is performed in a DEF demonstration kit. The updated results confirm that the optimum operating temperature of DEF is in low-temperature range where the ethanol crossing over the cell is compromised with the active-ions diffused process. The optimum operating temperature of 51°C is observed whereas cell temperature increases continuously with ethanol concentration. The DEF demonstration kit can achieve maximum current and power densities of 4.83 mA/cm² and 4.76 mW/cm², as respectively at a maximum ethanol concentration of 23.75 %vol. The results of this study indicate that there are some potentials on using DEF as a backup generator of VRE in Thailand. The DEF requires the shortest start-up period regarding its lowest operating temperature range (lowest warm–up period). Furthermore, the DEF uses sustainable renewable bio-ethanol, which is available in Thailand. In the same vein, the thermal efficiency of DEF is comparable to hydrogen fuel cell but provide easier to handle with (considered on storage, transport and distribution). The major limitation of this study is the up-scaling methodology, high cost of catalyst materials and management unit to matching the DEF with variable electricity.
load. Further work needs to be done to establish whether the DEFC technology can be applied in Thailand.

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