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Investigation of operating temperature effects on PEM fuel cell

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Abstract

In recent years, due to the negative effects of fossil fuels on the world such as the greenhouse effect and global warming, there has been an increasing interest in new alternative energy sources with their efficiency. Reducing or even eliminating these effects as much as possible will make our world more livable. Fuel cell systems, which are the new alternative energy system with almost zero harmful emissions, have been developed instead of fossil fuel-based systems. One of them is the proton exchange membrane (PEM) fuel cell. Although PEM fuel cell has significant advantages, it also has its disadvantages due to the cost and the difficulties in obtaining and storing hydrogen used as fuel. For these reasons, the efficiency of a PEM fuel cell is of great importance. The efficiency of fuel cells is significantly affected by different parameters. The most important of these parameters are the temperature, the electrochemical platinum surface areas of the cathode and anode layers, the partial pressures of reactant gases, and humidity. The operating temperature is effect directly the losses of activation and performance of fuel cell. In this study, the temperature effects are investigated on PEM fuel cell for performance and efficiency. Simulated typical polarization curves are performed for PEM fuel cell using the Polybenzimidazole and the Nafion membrane at different current densities. Increasing temperature in the fuel cell leads to an increase in fuel cell efficiency. A higher cell temperature increases the membrane conductivity and the exchange current density with an improvement of the cell behavior.

Keywords: PEM fuel cell, temperature, losses, efficiency

1. Introduction

A fuel cell is a high-efficiency electrochemical energy conversion device that can generate electricity and produce heat, with the help of a catalyst. Currently, the world's main source of energy is the burning of fossil fuels and the by-products of this combustion (eg SOx, NOx, CO2, and fine particles) seriously pollute the air, soil, and water [1-2].

While energy consumption continues to increase worldwide, unfortunately around 88% of the current energy economy is based on fossil fuels [3]. Nowadays, interest in alternative energy sources is growing rapidly due to reasons such as the depletion of fossil fuels, global warming, and climate change. Complete exhaustion or recovery of fossil fuels become unprofitable is only a matter of time. Despite their large share in the energy portfolio, the age of fossil fuels is coming to an end [4].

Some researchers have been focused on finding new alternative energy sources for many years, but some researchers have also focused on more environmentally friendly solutions such as renewable energy. Fossil fuels based energy resources are decreasing day by day, and existing solutions and resources for the future must be sustainable. One of these solutions is the proton exchange membrane fuel cell (PEMFC) fuel cell technology. Some fuel cells are commercialized, such as proton exchange membrane fuel cell (PEMFC), alkaline fuel cell (AFC), solid oxide fuel cell (SOFC), molten carbonate fuel cell (MCFC), and direct methanol fuel cell (DMFC).

Proton exchange membrane fuel cell (PEMFC) has become the most popular fuel cell among these fuel cell types due to it has small size, short start time, low noise, emissions, and high efficiency. FEM fuel cell is the most popular widely used in power plants, vehicles and vehicles combined cooling heating and power system of buildings [5-6]. Chen et al. (2017) presented parametric analysis and optimization of the PEM fuel cell system for maximum power and efficiency using a novel evolutionary algorithm and reached 79% of the system efficiency. Hydrogen-oxygen PEM fuel cells can be generally divided into two sorts in terms of the operating temperature, one of them is the low-temperature PEM fuel cell and the other is the high-temperature PEM fuel cell.

Some studies and researches have been conducted on

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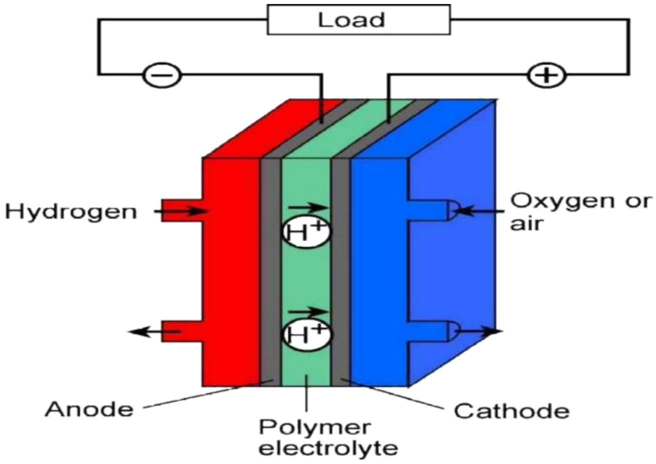
temperature effects on PEM fuel cell using a Nafion membrane as an electrolyte at low temperatures below 90 ℃ [8-17]. Their results showed that increasing temperature leads to an increase in fuel cell efficiency. Some studies and researches have been conducted on high-temperature temperature effects on PEM fuel cell using polymer electrolyte membrane such as Polybenzimidazole (PBI) doped polymeric, Sulfonated hydrocarbon polymers as an electrolyte at high temperatures above 120 ℃ [18-25]. As a result of investigating the effects of high temperature on the PEM fuel cell, it has been observed that a higher cell temperature increases the membrane conductivity and exchange current density with an improvement in cell behavior. Also, the high-temperature PEM fuel cell tolerance to CO is higher than in conventional Nafion-based PEM fuel cells.

2. PEM fuel cell

The various components of a simple fuel cell are shown in Figure 1. A single cell consists of two gas field flow plates, one for hydrogen and one for oxygen, separated by a membrane electrode assembly. The field flow plates contain channels to allow gases to be in contact with as much of the membrane electrode assembly as possible.

Figure 1. Schematic diagram of a simple PEM fuel cell.



As can be seen from the schematic diagram, while hydrogen molecules enter the anode side of the cell, oxygen enters the cathode side. In a reduction reaction, the hydrogen molecule releases its electrons flowing from the anode electrode via external electrical charge to the cathode electrode. It is this flow of electrons that we observe as electricity. Hydrogen protons flow through the ion-conducting membrane to the cathode. They combine with oxygen molecules and free electrons at the cathode to form water. The fuel cell electrochemically transformed hydrogen and oxygen gases into electricity and water. The overall reaction is hydrogen plus oxygen producing water.

Anode:

$$H_2 \rightarrow 2H^+ + 2e^- \text{ (oxidation)} \quad (1)$$

Cathode:

$$\tfrac{1}{2} O_2 + 2e^- + 2H^+ \rightarrow H_2O \text{ (reduction)} \quad (2)$$

Overall Reaction:

$$H_2 + \tfrac{1}{2} 0_2 \rightarrow H_2O + \text{Electrical Energy} \quad (3)$$

The enthalpy of this exothermic reaction is -285.8 kilojoules per mole PEM fuel cell electrochemical reactions. The ideal cell voltage (ΔE, reversible) can be calculated from Gibb's free energy (ΔG) equation as follows;

$$\Delta G = \Delta H - T\Delta S \quad (4)$$

$$\Delta E = - \Delta G/(nF) \quad (5)$$

Where ΔH is the total enthalpy of the reaction, ΔS is the total entropy of the reaction, n is the number of electrons that pass through the system per molecule of reactant, n is the number of electrons that pass through the system per molecule of reactant and F is Faraday's constant (96485 Coulombs/mole).

3. Effect on parameters on PEM fuel cell

Hydrogen-oxygen PEM fuel cells can be generally divided into two sorts in terms of the operating temperature that are low-temperature PEM fuel cell and high-temperature PEM fuel cell. The PEM fuel cell operating temperature is mainly controlled or limited by the thermostability and activity of the electrolyte. Low-temperature PEM fuel cell using Nafion membrane as an electrolyte is operated below 90 ^{o}C while high-temperature PEM fuel cell using polybenzimidazole doped polymeric membranes with phosphoric acid (PBI/H_3PO_4) as an electrolyte is operated above 120 ^{o}C [18].The parameters of conditions such as temperature, platinum surface areas both of the cathode and anode layers, the partial pressures of reactant gases, the gas diffusion layer properties, different membrane thickness, path of the reactant flow, and humidity lead to change the activation and the cell performance. Variations of the physical properties of these parameters may affect the performance, durability, and reliability of the fuel cell operation.

4. Operating temperature effects on PEM fuel cell

The operating cell temperature is a very important parameter because it has a great effect on both PEM fuel cell electric and thermal efficiencies: the electric power generated and the quality of the heat available for cogeneration depend on it. The limit ideal cell voltage equals is 1.23 V and the efficiency limit can be calculated to 83% at 25 ℃ room temperature and standard atmospheric pressure (ΔG= -237.2 kJ at 25 ^{o}C). Gibbs free energy is temperature-dependent whereas the specific change of enthalpy is constant for the reaction. Gibbs free energy is -228.200 kJ and the limit ideal cell voltage equals is 1.18 V at 80 ℃ of operating temperature. As the operating temperature increases, the ideal voltage of the fuel cell (reversible) decreases theoretically as shown in Figure 2.

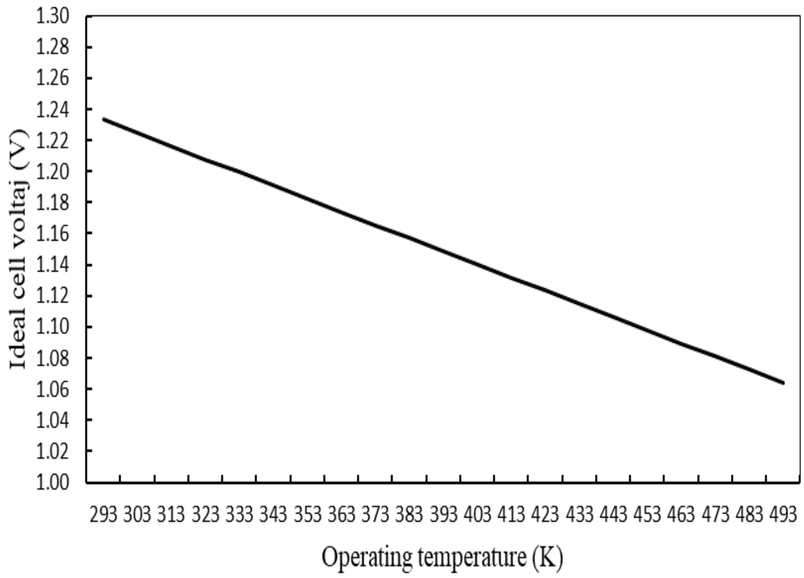


Figure 2. Ideal cell voltage at different operating temperatures.

Generally, the theoretical voltage of a fuel cell operating below 90 ^{o}C is about 1.23 V. In practice, this voltage is less than its theoretical value due to some voltage losses that affect the reversible voltage-current density curve as show shown in Figure 3.

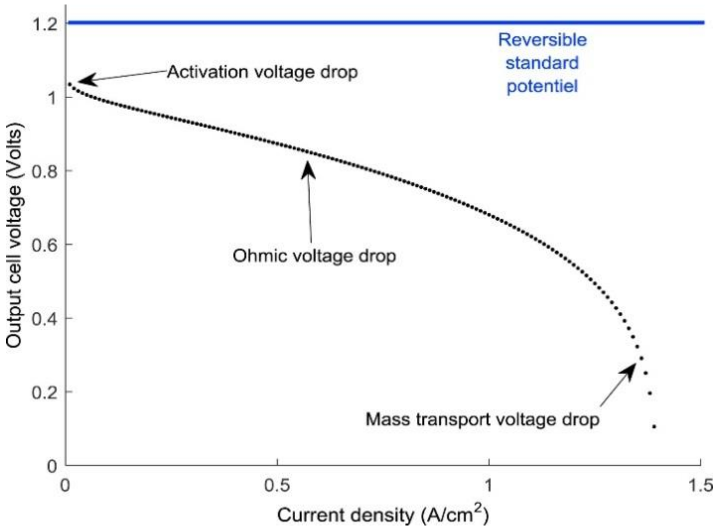


Figure 3. The reversible current density curve for PEM fuel cell indicating the principal areas of voltage losses occurrence [13].

PEM fuel cell operating temperature is between 60 ºC and 80 ºC for conventional use Nafion and the Polybenzimidazole (PBI) membrane, titanium PBI-based composite membrane between 120 °C and 200 °C [19, 25].

During electrochemical reactions and electron transfer processes, an electromotive force is generated between two electrodes. Assuming the operating conditions of a single fuel cell are the hydrogen purity of 100%, and the Air's composed of 21% oxygen and 79% nitrogen in the fuel cell. The output voltage of a single cell can be written as follows [26].

$$V_{cell} = E_{Nernst} - V_{act} - V_{ohmic} - V_{concent} \qquad (6)$$

where E_{Nernst} is Nernst potential, V_{act} is activation polarization loss, V_{ohmic} is losses are associated with electron and ion conduction processes occurring in the electrodes, electrolyte, and interconnects resistances across each material interface, and $V_{concent}$ is concentration losses.

The calculation formulas of Equation (6) terms are shown in Equations 7-10:

$$E_{Nernst} = 1.229 - 0.000846(T - 298.15) + 0.0000431T\left[\ln\left(P_{H_2} - P_{O_2}^{1/2}\right)\right] \qquad (7)$$

$$V_{act} = \varepsilon_1 - \varepsilon_2 T - \varepsilon_3 T ln\left(C_{O_2}\right) + \varepsilon_4 T ln(I_c) \qquad (8)$$

$$V_{ohmic} = I_c t_m \left[\frac{181.6\left[1+0.03\left(\frac{I_c}{A}\right)+0.062\left(\frac{T}{303}\right)^2\left(\frac{I_c}{A}\right)^{2.5}\right]}{A\left[\lambda-0.634-3\left(\frac{I_c}{A}\right)\exp(4.18(\frac{T-303}{T}\right]}\right] \qquad (9)$$

$$V_{concent} = -\frac{RT}{nF}\ln\left(1 - \frac{J}{J_{max}}\right) \qquad (10)$$

where T is the operating temperature of PEM fuel cell, P_{H_2} and P_{O_2} is are the pressures of hydrogen and oxygen reacted in PEM fuel cell at atmospheric pressure, ε_1, ε_2, and ε_3 are empirical coefficients determined by electrochemistry and thermodynamics equations, C_{O_2} is oxygen concentration on cathode catalyst layer, I_c is current, t_m is membrane thickness, A is cell active area, λ is a semiempirical parameter representing the effective water content of the membrane, J is current density, n is the number of equivalents involved in a reaction.

Thermal (P_{therm}) and the electrical power (P_{elec}) of a single fuel cell can be shown as follows [7]:

$$P_{therm} = I_c(LHV - V_{cell}) \qquad (11)$$

$$P_{elec} = I_c V_{cell} \qquad (12)$$

where LHV is the equal voltage of the lower heating value of hydrogen. Thermal (η_{therm}) and the electrical efficiency (η_{elec}) of a single fuel cell can be shown as follows:

$$\eta_{therm} = \frac{1}{S_{H_2}}\left(1 - \frac{V_{cell}}{LHV}\right) \qquad (13)$$

$$\eta_{elec} = V_{cell}/S_{H_2}LHV \qquad (14)$$

where S_{H_2} is hydrogen stoichiometry

Simulated typical polarization curves for PEM fuel cell using the PBI membrane operating at 120 ºC and for PEM fuel cell using the Nafion membrane operating at 70 ºC taken from Zhang et al (2007) and

Jung et al (2012) respectively are shown in Figure 4. The authors were intended to cell temperature distribution in the membrane electrode assembly and they were performed on the temperature distribution throughout the membrane electrode assembly and the effect of Nafion thickness on cell temperature distribution [15].

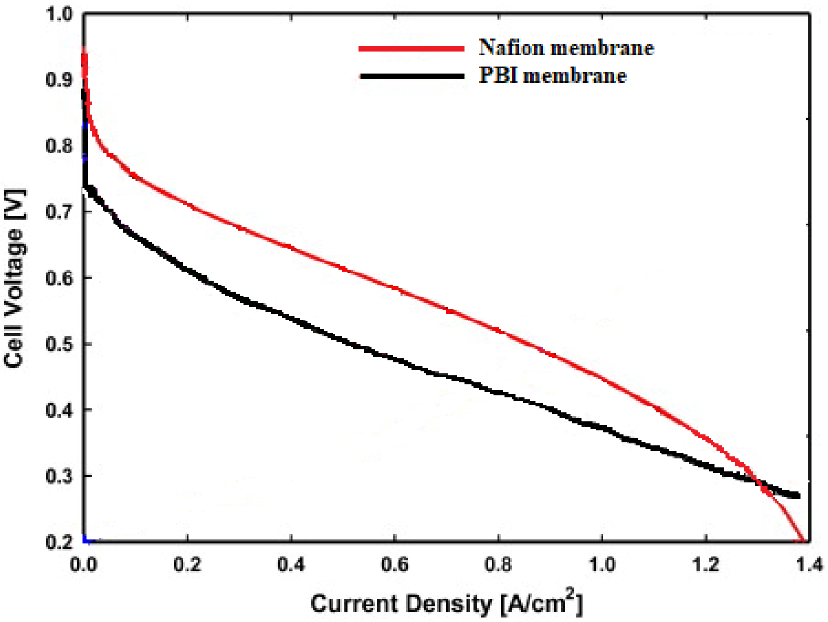


Figure 4. Typical polarization curves for PEM fuel cell using the PBI membrane operating at 120 ^{o}C [19], and PEM fuel cell using the Nafion membrane operating at 70 ^{o}C [15].

Santarelli et al. (2007) presented an experimental analysis of the effects of the operating variables on the performance of a single PEMFC and approved that an increase of the temperatures improves the behavior of the cell using a Nafion membrane at low temperature in Figure 5.

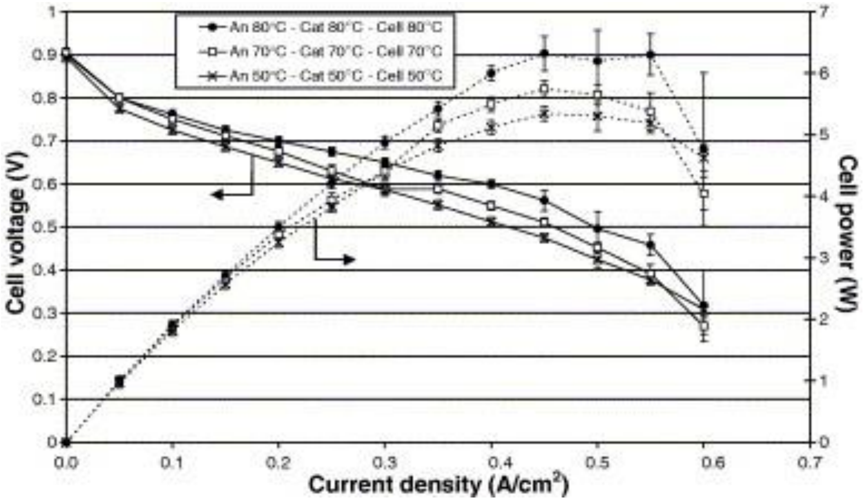


Figure 5. Polarization (solid lines) and power (dotted lines) curves at constant temperatures [8].

Thermodynamic irreversibilities in the PEM fuel cells decrease with a rise of cell operating temperature. In order to reduce thermodynamic irreversibilities of PEM fuel cell should be operated at higher operating temperature and pressure with the membrane thickness should be reduced.

Ven et al. (2013) investigated Nafion 117 and the ionic liquid doped polybenzimidazole membranes (PBI/IL) for low-temperature and high-temperature PEM fuel cell applications respectively [27]. They showed H_2-O_2 polarization curves as a function of the operating temperature without humidification for a) Nafion 117 and b) PBI/IL membranes in Figure 6a and Figure 6b.

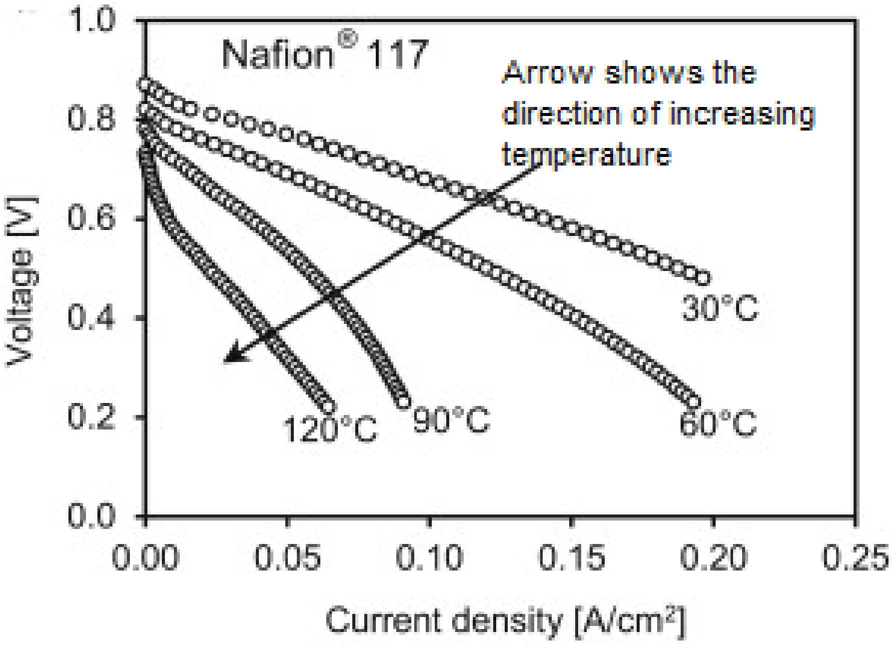


Figure 6a. H_2-O_2 polarization curves as a function of the operating temperature without humidification for Nafion 117 [27].

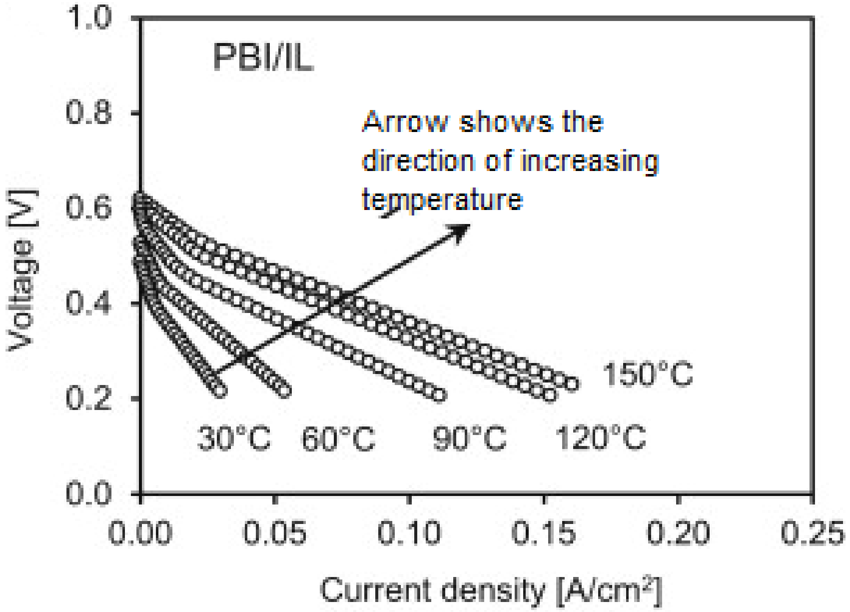


Figure 6b. H_2-O_2 polarization curves as a function of the operating temperature without humidification for PBI/IL [27].

The performance of Nafion membrane 117 decreases with increasing operating temperature and the performance of PBI/IL membranes increases with increasing operating temperature in Figures 6a and 6b respectively

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5. Conclusions and discussion

The following conclusions can be drawn:

- As the current density increases due to the electrochemical reaction, the temperature difference between the anode and cathode increases.
- As the thickness of Nafion increases due to heat accumulation, the cell temperature at the cathode increases. but the cell temperature distributions are similar to the anode.
- A higher cell temperature increases the membrane conductivity and the exchange current density with an improvement of the cell behavior.
- An increase in reactive saturation temperature

leads to better performance, especially in the case of low and medium loads.

- In the high-temperature PEM fuel cell, the CO adsorption on the anode catalyst is less favored and the tolerance to CO is higher than in conventional Nafion-based PEM fuel cells.
- The high-temperature PEM fuel cell is accelerated reaction kinetics at the electrodes that it can allow platinum to be replaced by more economical catalysts.
- The high-temperature PEM fuel cell has simpler water management because the presence of liquid water can be neglected. Also, high-temperature waste heat availability for cogeneration applications.

It is suggested that the effect of the temperature results on the practical operation and commercial cells available on the market of the fuel cell to analyze their performance at real different operating conditions.

Current SCM practices are not capable of meeting the construction industry's needs. Delivering materials on time determines whether the project to be completed on time or not, and current practices in construction should change in order to achieve these goals [11–14].

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