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Performance characteristics of direct formic acid fuel cell (DFAFC) by using Pt-based binary metal alloy supported on activated carbon as anode catalysts

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ABSTRACT

Direct formic acid fuel cell (DFAFC) system with hydrogen peroxide (H_2O_2) used instead of oxygen as cathode oxidant for marine applications was investigated. Cell performance of DFAFC system was studied on various types of metal (M): Ir, Mo, Co, Ag, W, Ni, Sn of Pt-M binary metal alloy at anode side. The anode catalysts were prepared by using an airbrush painting method. Performance characteristics of DFAFC system such as electrical and thermal power and cell potential were also studied and compared between experiment and computation by using DFAFC stack model.

The 15%Pt-15%Sn/C catalyst yielded 17% lower catalytic activity for the formic acid oxidation reaction than the 20%Pt-10%Ru/C commercial catalyst but gave higher open circuit voltage. In addition, the price of 15%Pt-15%Sn/C was about 50% cheaper than the 20%Pt-10%Ru/C commercial catalyst. The polarization curve of experimental results was compared to computational results. A good agreement is found between experiment data and computation.

Key Words: *Direct formic acid fuel cell (DFAFC), Pt-based binary metal alloy, Anode catalyst, Performance characteristics.*

1. Introduction

Fuel cells have been considered as an important power source in the future because of high energy conversion efficiency and low environmental pollution. Proton exchange membrane fuel cells (PEMFC) have been commonly used with low-temperature operating system. There is one subcategory of direct proton exchange membrane fuel cell (PEMFC): direct liquid fuel cells. The direct liquid fuel cell consisted of direct methanol fuel cell (DMFC) and direct formic acid fuel cell (DFAFC). Both of them use different fuel instead of H_2: methanol (CH_3OH) for DMFC and formic acid (HCOOH) for DFAFC. [1-4]

The direct liquid fuel cells, the DMFC has some disadvantages [5, 6]. Firstly, methanol is easy to penetrate the Nafion membrane, causing the decrease in the DMFC performance by this crossover of fuel. Secondly, the electro catalytic activity of Pt usually used as the anodic catalyst in DMFC is low and also Pt is easy to be poisoned with CO as an intermediate of the methanol oxidation.

Formic acid has recently appealed attention as an alternative fuel for the direct liquid fuel cells. Many advantages of formic acid have been superior to hydrogen and methanol: Formic acid is liquid at room temperature and the dilute formic acid is the generally safe food additive on the US Food and Drug Administration list [5, 6]. It is inflammable and thus its storage and transport are safe. Whereas this fuel is strong electrolyte, proton is better transported at the anode compartment of fuel cell system [7, 9, 10]. The fuel gives two orders of magnitude smaller crossover flux through a Nafion membrane than methanol [8, 11, 12]. Formic acid also has the theoretical electronic motive force calculated from the Gibbs free energy higher than both hydrogen and direct methanol fuel cells [5, 9]. Catalysts play a significant role to accelerate chemical reaction rate. Platinum-Ruthenium catalyst supported on carbon (Pt-Ru/C) is commonly used for DFAFC system. However, the cost of this type of catalyst is quite expensive. Then, the development of fuel cell system's catalyst will be advantage to decrease the cost of catalyst.

In this research work, direct formic acid fuel cell (DFAFC) system with hydrogen peroxide (H_2O_2) used instead of oxygen as cathode oxidant for marine applications was studied. Cell performance of DFAFC system was examined on varying different types of metal (M): Ir, Mo, Co, Ag, W, Ni, Sn of Pt-M binary metal alloy at anode side. Performance characteristics of DFAFC system such as electrical and thermal power and cell potential were also investigated and compared between experiment and computation by using DFAFC stack model.

2. Description of experimental set up

2.1 Materials

All chemical used in this research is analytical grade. The 35 wt% Hydrogen peroxide, 98-100% Formic acid and 30 wt% sulfuric acid were purchased from AppliChem. Vulcan XC72 carbon (325 mesh) was procured from Cabot company. The 5 wt% Nafion solution or perfluorosulfonic acid-PTFE copolymer, 0.180 mm thick Nafion® membrane, Platinum black, PtRu on carbon black, Iridium black, 99.8% (metals basis), Molybdenum powder, APS 3-7 micron, 99.95% (metals basis), Cobalt powder, 1.6 micron, 99.8% (metals basis), Silver powder, APS 4-7 micron, 99.9% (metals basis), Tungsten powder, APS 1-5 micron, 99.9% (metals basis), Nickel powder, APS 3-7 micron, 99.9% (metals basis) and Tin powder, 325 mesh, 99.8% (metals basis) were purchased from Alfa Aesar.

2.2 Preparation of catalyst ink

The preparation method of the catalysts is as follows: 30%Pt/C catalyst: 150 mg Platinum black (HiSPEC^{TM} 1000) and 350 mg Vulcan XC-72 carbon; were added into 10 mL Millipore water. After that 5.3 ml of 5 wt% Nafion solution was added into the above solution. The suspension was stirred for 3 days at room temperature. The preparation method of other catalysts is as same as the above mention. Only the components of the metals and Vulcan XC-72 carbon were different as follows. The 20%Pt-10%Ru/C catalyst: 500 mg Platinum/Ruthenium (nom. 20%/10%) on carbon black (HiSPEC^{TM} 5000); 20%Pt-10%M/C (M = Ir, Mo, Co, Ag, W, Ni and Sn): 100 mg Platinum black (HiSPEC^{TM} 1000), 50 mg Ir, Mo, Co, Ag, W, Ni or Sn metal and 350 mg Vulcan XC-72 carbon; 15%Pt-15%Sn/C catalyst: 75 mg Platinum black (HiSPEC^{TM} 1000), 75 mg Sn metal and 350 mg Vulcan XC-72; 10%Pt-20%Sn/C catalyst: 50 mg Platinum black (HiSPEC^{TM} 1000), 100 mg Sn metal and 350 mg Vulcan XC-72 carbon.

2.3 Preparation of Nafion membrane

A 6.25 cm^2 Nafion® membrane, 0.180 mm thick (Nafion N-117 perfluorosulfonic acid-PTFE copolymer) was boiled in 150 ml of 3 wt% H_2O_2 solution at 363 K for 60 minutes. Then, H_2O_2 was rinsed. Next, it was boiled in a 150 ml of Millipore water at 363 K for 60 minutes. Again rinsed the membrane in Millipore water for four times, and boiled it in a 150 ml of 3 wt% H_2SO_4 aqueous solution at 363 K for 60 minutes. After that, the membrane sheet was boiled again in a 150 ml of Millipore water at 363 K for 60 minutes and rinsed with Millipore water for four times. Finally, the membrane sheet was dipped in Millipore water overnight.

2.4 Airbrush painting procedure

The membrane electrode assemblies (MEA) were fabricated in house using an 'airbrush painting' technique to apply the catalyst layers. After the last step of preparation, the membrane sheet had to be dried for 30 minutes at 383 K prior to use with airbrush painting. Both the anode and cathode catalyst inks were directly sprayed using an airbrush gun onto either side of the membrane sheet at 403 K. The catalyst loading for anode and cathode was approximately 10 mg/cm^2. The composition of anode and cathode catalyst used in this study is 20%Pt-10%Ru/C or 20%Pt-10%M/C and 30%Pt/C, respectively.

2.5 Single-direct formic acid fuel cell test

The designed single-cell test apparatus is built in house and used for formic acid fuel cell (Fig 1). The anode/cathode flow fields are in direct contact with the diffusion layer which distributes the reactants from the flow field towards the catalyst layer. The 10% formic acid/17.5% hydrogen peroxide enters the cell at a flow rate of 2 mL min^{-1} through plastic fittings, directly into the anode/cathode sides on membrane. The MEA is sandwiched between the two flow fields and sealed with gaskets. Different catalyst, such as 20%Pt-10%Ru/C and 20%Pt-10%Mo/C were used for the anode catalyst and 30%Pt/C was used for the cathode catalyst. The cell performance was evaluated at room temperature with a PC-card of Heliocentris Company which recorded the cell voltage, the current, and the power via program h-tec fuel cell monitor 2.0 under characteristic automatically mode.

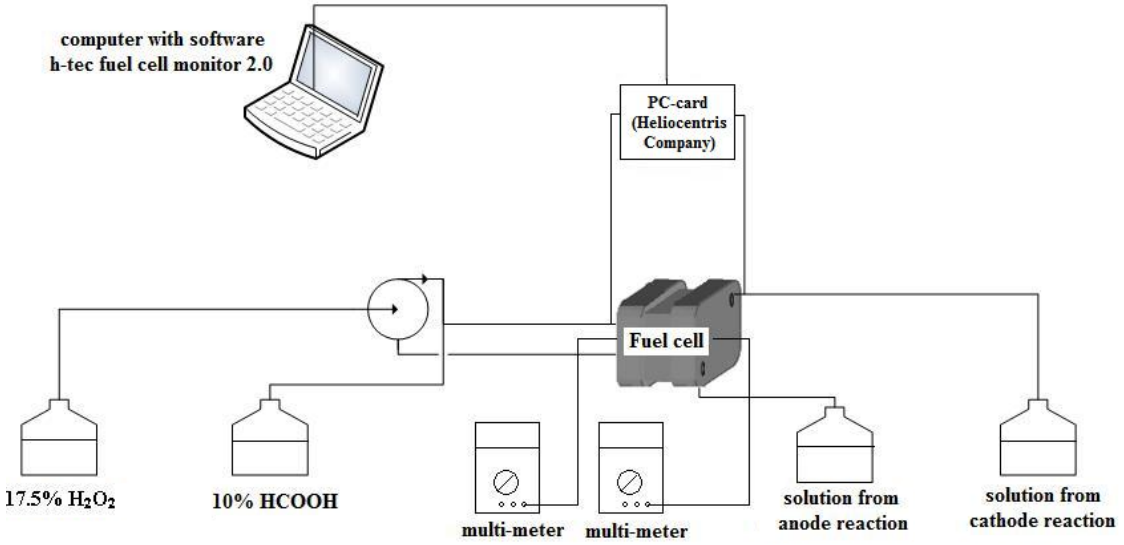


Fig 1. Schematic diagram of single-direct formic acid fuel cell test stand at Leibniz Institute for Catalysis at the University of Rostock, Germany

3. DFAFC stack model

Direct formic acid fuel cell is the system converting chemical energy to be electrical energy. The electrochemical reaction at anode and cathode of a liquid-liquid DFAFC can be expressed as follows:

Anode: $HCOOH \rightarrow CO_2 + 2H^+ + 2e^-$ (E^0 = -0.2 V)

Cathode: $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ (E^0 = 1.78 V)

Input parameters are current and number of cells. Output characteristic of fuel cell shows correlation between cell voltage and current. The regression model of I-V curve used in this research is the 5th degree polynomial curve fitting from CurveExpert 1.3 program. MATLAB/simulink environment is used to be an effective tool to calculate many parameters including system efficiency. Mathematical equations involving with model can be written as follows [13]:

3.1 Heat produced

Heat is produced when a fuel cell operates. As electrochemical reaction of system mentioned above, the reversible standard potential (E_o) is 1980 mV per mole of formic acid (HCOOH) at 25 °C. The E_o is determined from the change in the Gibb's free energy when vapor water is produced. For a stack of n cells at current I, the amount of heat produced (P_{therm}) can be written as

$$P_{therm} = \frac{n \times I \times (1980 - U_c)}{1000} \quad \text{[mW]} \qquad (1)$$

Where n are numbers of cells, I is the current of single cell in unit mA and U_c is the voltage of a single cell in unit mV.

3.2 Electrical power

For electric power (P_{el}) of a whole fuel cell stack in unit milli-watt (mW) is

$$P_{el} = \frac{n \times I \times U_c}{1000} \quad \text{[mW]} \qquad (2)$$

3.3 Voltage of stack

The voltage of a whole fuel cell stack (U_{stack}) can be calculated from

$$U_{stack} = n \times U_c \quad \text{[mV]} \qquad (3)$$

3.4 Efficiency of fuel cell

The efficiency of a working fuel cell (η) can be defined as follows

$$\eta = \frac{U_c \times 100}{1980} \quad \text{[\%]} \qquad (4)$$

3.5 Formic acid (HCOOH) usage

From anode reaction, there are two electrons from each mole of formic acid. Therefore, the equation for stack of n cells is

$$\text{HCOOH usage} = \frac{I \times n \times 1000}{2F} \quad \text{[mole s}^{-1}\text{]}$$

Where F is Faraday’s constant which equals to 96500 C.

The molar mass of formic acid is 46.03×10^{-3} kg mole^{-1}, then

$$\begin{aligned} \text{HCOOH usage} &= \frac{46.03 \times 10^{-3} \times I \times n \times 1000}{2F} \quad \text{[kg s}^{-1}\text{]} \\ &= 2.38 \times 10^{-4} \times I \times n \quad \text{[kg s}^{-1}\text{]} \qquad (5) \end{aligned}$$

3.6 Hydrogen peroxide (H_2O_2) usage

From cathode reaction, two electrons are transferred for each mole of hydrogen peroxide. Then, the equation for a stack of n cells is

$$H_2O_2\text{ usage} = \frac{I \times n \times 1000}{2F} \qquad [\text{mole s}^{-1}]$$

The molar mass of oxygen is 34.02×10^{-3} kg mole^{-1}, then

$$H_2O_2\text{ usage} = \frac{34.02 \times 10^{-3} \times I \times n \times 1000}{2F} \qquad [\text{kg s}^{-1}]$$

$$= 1.76 \times 10^{-4} \times I \times n \qquad [\text{kg s}^{-1}] \qquad (6)$$

3.7 Water production

In a DFAFC, water is produced at the rate of one mole for every one electron. Then, for stack of n cells, the water production is

$$\text{Water production} = \frac{I \times n \times 1000}{F} \qquad [\text{mole s}^{-1}]$$

The molecular mass of water is 18.02×10^{-3} kg mole^{-1}, then

$$\text{Water production} = 1.87 \times 10^{-4} \times I \times n \qquad [\text{kg s}^{-1}] \qquad (7)$$

4. MATLAB/Simulink computation procedure

The general model structure is shown in Fig. 2. Current (I) and number of cell (n) are input parameters while output parameters are heat produced (P_{therm}), electrical power (P_{el}), voltage of stack (U_{stack}), efficiency of fuel cell (η), formic acid usage, hydrogen peroxide usage and water production. The output polarization curve characterizes the performance of fuel cell based on electrochemical processes. Fig. 3 displays the block diagram of MATLAB/Simulink for a DFAFC system. Coefficients, a-f, are obtained from regression analysis with the 5th maximum power of polynomial equation fitting.

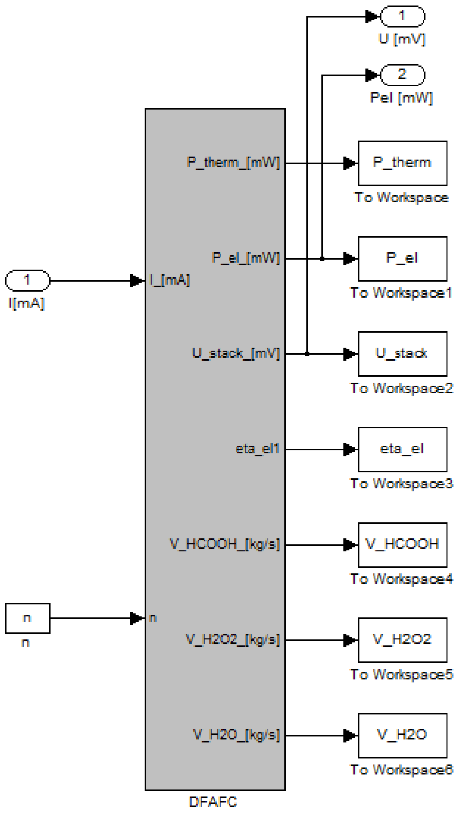


Fig 2. General model structure of DFAFC system using MATLAB/Simulink

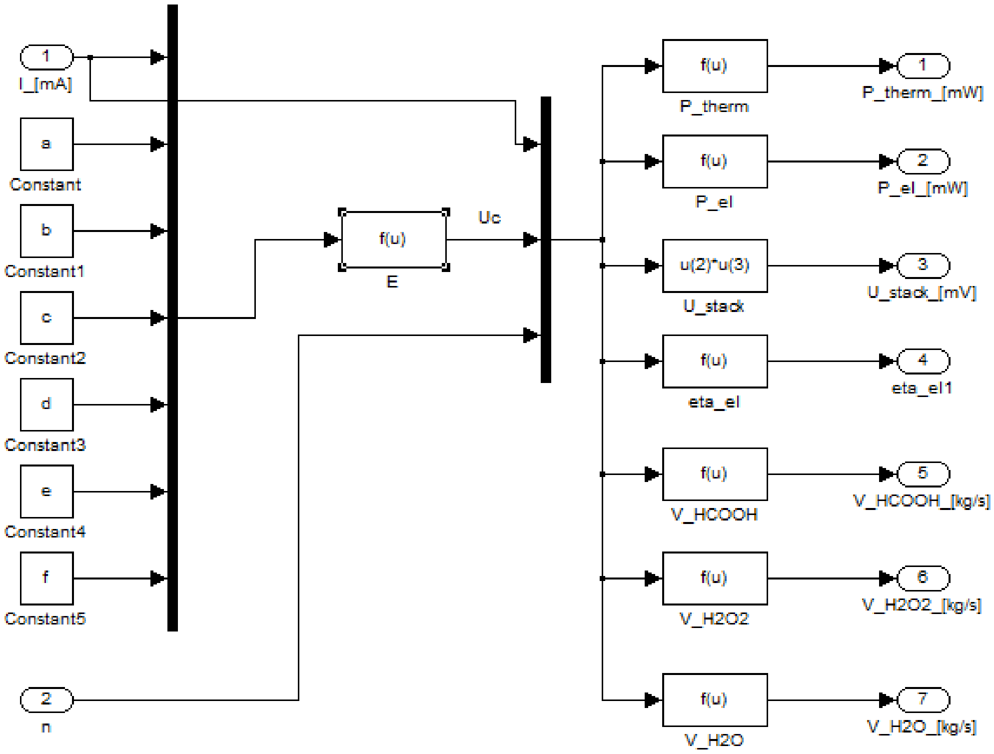


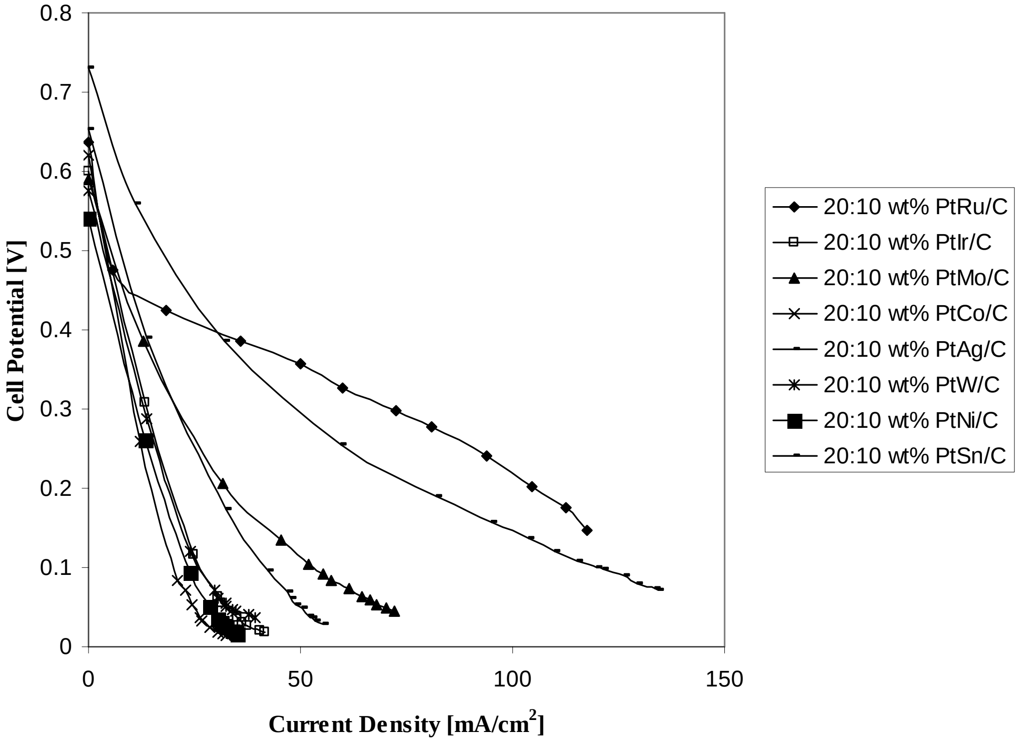
Fig 3. Block diagram of DFAFC system using MATLAB/Simulink

5. Results and discussion

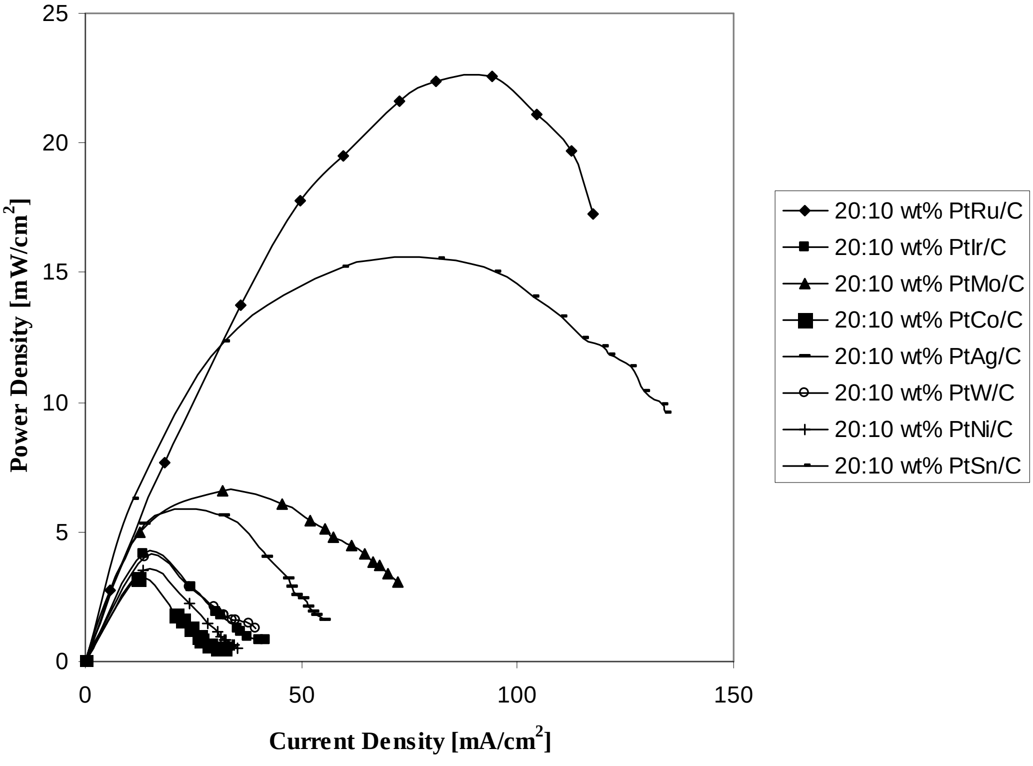
5.1 Experimental results

Fig 4A illustrates the effect of anode catalyst composition on the cell polarization curve profile. Eight bimetallic metal anode catalysts were tested: Pt-Ru/C; Pt-Ir/C; Pt-Mo/C; Pt-Co/C; Pt-Ag/C; Pt-W/C; Pt-Ni/C; and Pt-Sn/C. It is noted that types of catalyst affecting the open circuit voltage. For example, the open circuit voltage is 0.64 V for commercial Pt-Ru/C, 0.65 V for Pt-Ag/C and 0.55 V for Pt-Ni/C. Maximum open circuit voltage is 0.73 V for Pt-Sn/C as compared to other catalysts.

From the results of Fig 4A, Fig 4B is plotted between power density and current density. Maximum power densities obtained at any current densities for eight catalysts are: 23 mW/cm^2 at 94 mA/cm^2 for commercial Pt-Ru/C; 4 mW/cm^2 at 14 mA/cm^2 for Pt-Ir/C; 7 mW/cm^2 at 34 mA/cm^2 for Pt-Mo/C; 3 mW/cm^2 at 12 mA/cm^2 for Pt-Co/C; 6 mW/cm^2 at 24 mA/cm^2 for Pt-Ag/C; 4 mW/cm^2 at 16 mA/cm^2 for Pt-W/C; 4 mW/cm^2 at 15 mA/cm^2 for Pt-Ni/C and 16 mW/cm^2 at 82 mA/cm^2 for Pt-Sn/C. It can be seen that the 20%Pt-10%Sn/C as anode catalyst exhibits 30% lower catalytic activity than the 20%Pt-10%Ru/C commercial catalyst under the same operating conditions of DFAFCs. More precisely, Pt-Sn/C electrocatalysts shows a better activity when compared to the other catalysts. In order to find the optimal weight percentage ratio between Pt and Sn in the Pt-Sn/C catalyst, few catalysts with different Pt/Sn ratios are tested in single direct formic fuel cells. It is found that the ratio between Pt and Sn affects the fuel cell performance. The 15%Pt-15%Sn/C gives maximum power density of 19 mW/cm^2 at 84 mA/cm^2. The 15%Pt-15%Sn/C catalyst exhibits only 17% lower catalytic activity for the formic acid oxidation reaction than the 20%Pt-10%Ru/C commercial catalyst. Although 15%Pt-15%Sn/C catalyst cannot compete with the commercial catalyst in term of catalytic activity, the price of 15%Pt15%Sn, which is calculated from the metal's price of Alfa Aesar A Johnson Matthey Company, is about 50% cheaper than the commercial catalyst. Fig 5 shows effect of varying weight percentage ratio between Pt and Sn on cell performance.



(A)



(B)

Fig 4. Effect of different anode catalysts on the performance of single DFAFC at room temperature, 2 ml min^{-1} of 10 % Formic acid and 2 ml min^{-1} of 17.5% Hydrogen peroxide: (A) polarization and (B) power density curves

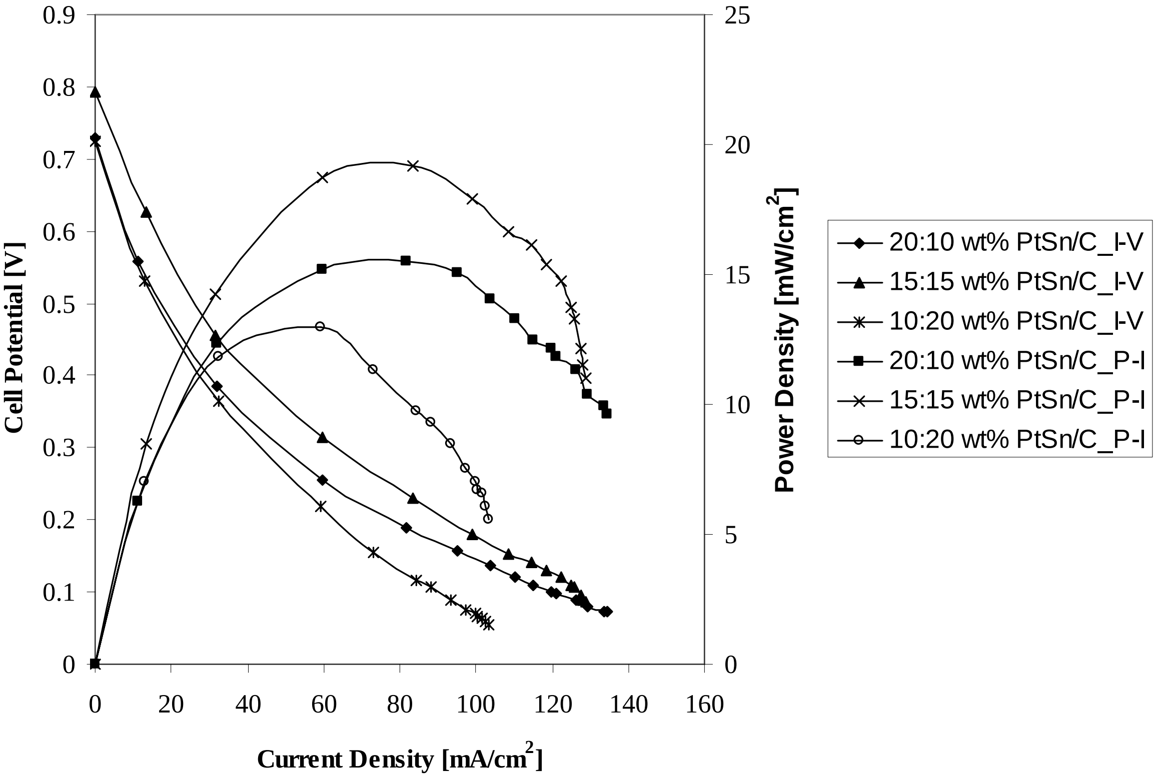


Fig 5. Effect of varying weight percentage ratios of Pt and Sn: 10:20, 15:15 and 20:10 on cell performance of DFAFC at room temperature, 2 ml min^{-1} of 10 % Formic acid and 2 ml min^{-1} of 17.5% Hydrogen peroxide

5.2 Computational results

This part will demonstrate only the result of 20%Pt-10%Ru/C as anode catalyst in single DFAFC test. From fitted curve, the 5th degree polynomial fitting shows standard error of 13.5022199 and correlation coefficient of 0.9978653. Fig 6 shows comparison of I-V curve between experiment and computation in single DFAFC system using 20%Pt-10%Ru/C as anode catalyst and 30%Pt/C as cathode catalyst.

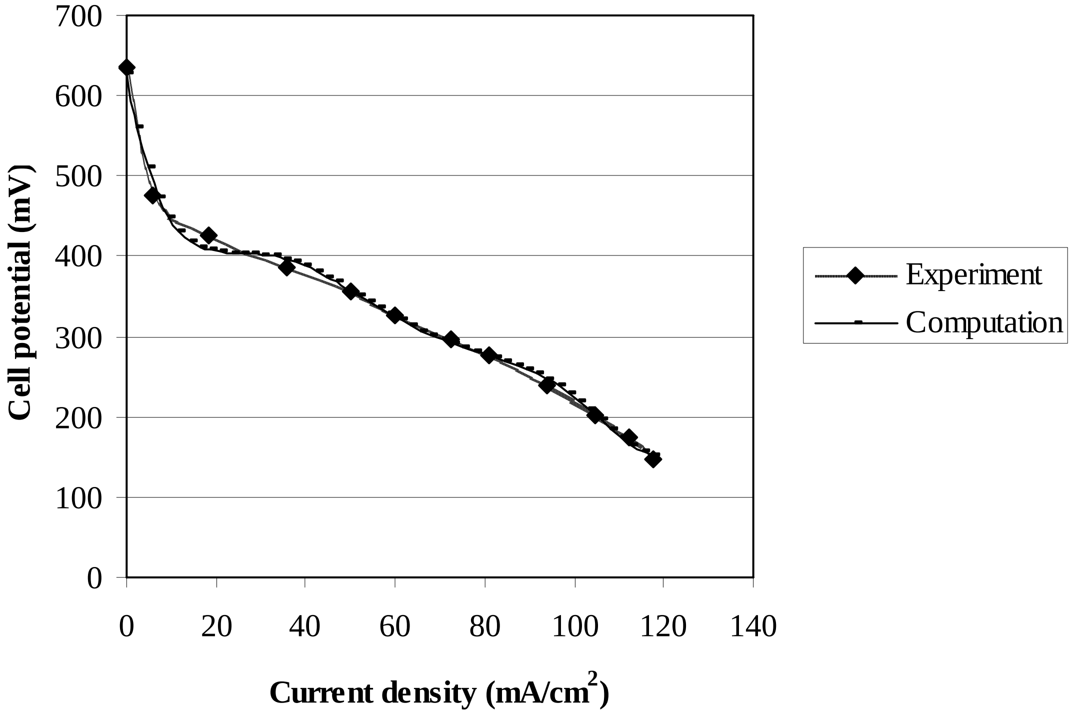


Fig 6. Comparison of I-V curve between experiment and computation using 20%Pt-10%Ru/C as anode catalyst and 30%Pt/C as cathode catalyst in single DFAFC system

As shown in Fig 7, the results of P_{el}, P_{therm} and η, that is computed by the DFAFC stack model, are plotted with current. Formic acid and hydrogen peroxide usage and water production are also computed as shown in Fig 8.

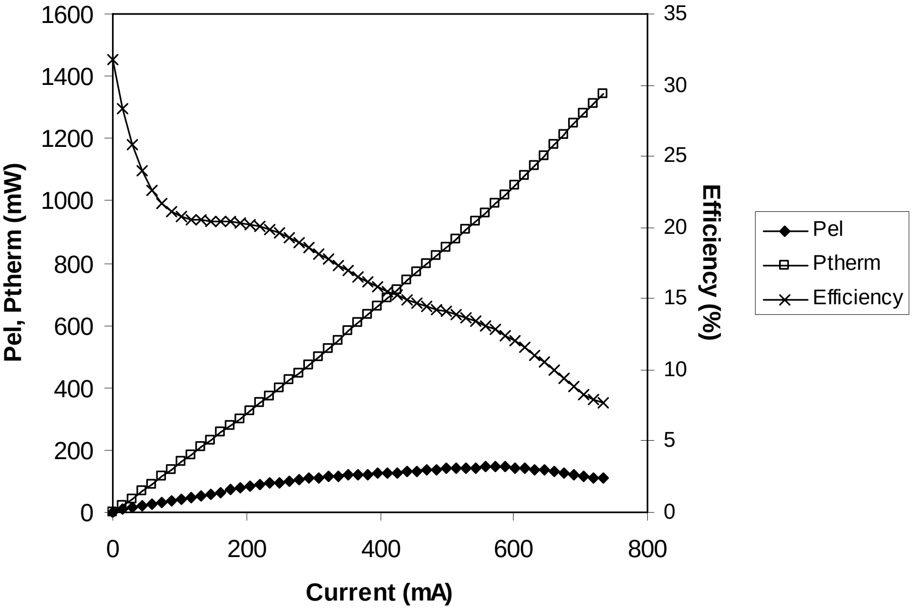


Fig 7. Effect of current on electrical and thermal power and efficiency

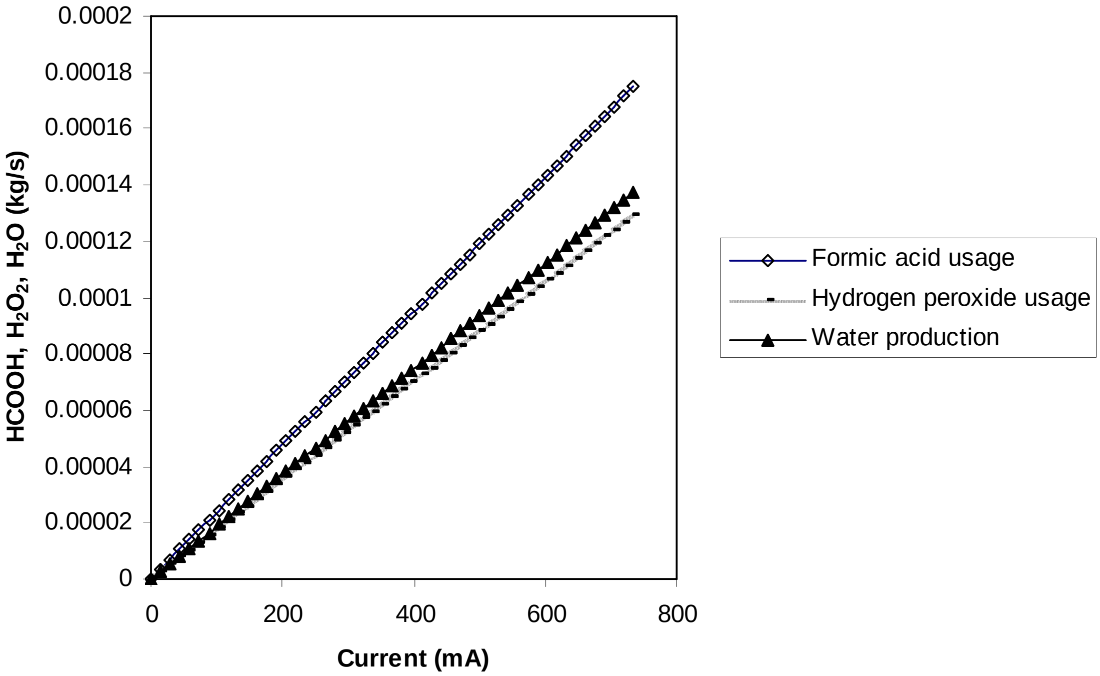


Fig 8. Effect of current on fuel and oxidant usage and water production

6. Conclusion

Direct formic acid fuel cell (DFAFC) system with hydrogen peroxide (H_2O_2) as cathode oxidant for marine applications is studied. Cell performance of DFAFC system is studied on varying different types of metal (M): Ir, Mo, Co, Ag, W, Ni, Sn of Pt-M binary metal alloy at anode side. The anode catalysts were prepared by using an airbrush painting method. Performance characteristics of DFAFC system such as electrical and thermal power and cell potential are also studied and compared between experiment and computation by using DFAFC stack model.

The 15%Pt-15%Sn/C catalyst yields 17% lower catalytic activity for the formic acid oxidation reaction than the 20%Pt-10%Ru/C commercial catalyst but gives higher open circuit voltage. In addition, the price of 15%Pt-15%Sn/C is about 50% cheaper than the 20%Pt-10%Ru/C commercial catalyst. Based on computational results of DFAFC stack model, the optimal current of DFAFC by using commercial Pt-Ru/C as anode catalyst and 30% Pt/C as cathode catalyst ranged from 200 to 300 mA. The cell efficiency varying from 18 to 20% is obtained at optimum operating condition. The water production rate of the system at optimum operating condition ranges from 4×10^{-5} to 5.5×10^{-5} kg/s. The polarization curve of experimental results is compared to computation results from model. A good agreement is found between experiment and computation.

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