

Dissertation Abstract

Study on the non-precious metal catalyst for cathode in a direct formic acid fuel cell

直接ギ酸形燃料電池のカソード用非貴金属触媒に関する
研究)

専攻 (Division) : Mechanical Science and Engineering

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Abstract

Non-precious metal catalysts (NPMCs) based such as iron (Fe) and cobalt (Co) catalysts have been widely studied in direct liquid fuel cells (DLFCs) application as cathode catalyst for oxygen reduction reaction (ORR), especially in direct methanol fuel cells (DMFCs). However, the performance of the single DMFC operation using the NPMCs at the cathode is remains low as compared with the conventional Pt/C catalyst. Therefore, the aim of this study is to achieve high performance in DLFC by applying the NPMC to the direct formic acid fuel cell (DFAFC) cathode. Fe- and Co-nitrogen doped-carbon nanotubes (NCNT) catalysts were synthesized and their ORR activity in acidic and alkaline medium was measured. As the application of such NPMC for DFAFC operation has not yet been reported, the fuel tolerance on the synthesized catalysts were investigated. Further, their performance in single DFAFC operation was evaluated and compared with the conventional Pt/C catalyst as well as the other DLFC operations. Fe-NCNT and Co-NCNT catalyst synthesized showed better fuel tolerance than the commercial Pt/C catalyst in both acidic and alkaline medium. In single DFAFC operation using both NPMCs in the cathode, higher performance achieved as compared with the other DLFCs reported in literatures.

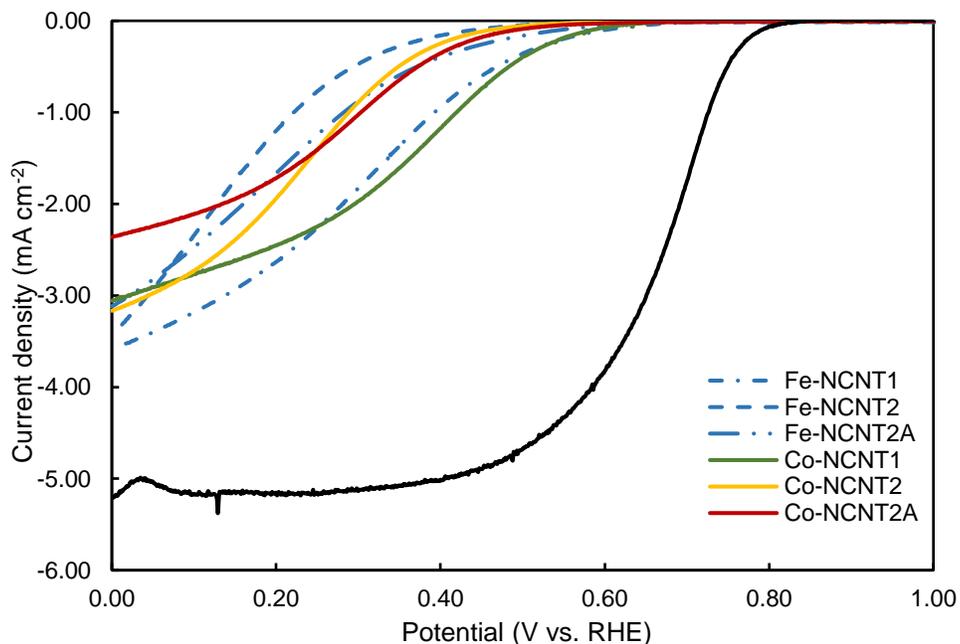
Direct liquid fuel cells (DLFCs) are one of polymer-electrolyte membrane fuel cell (PEFC) type that are recently gain more interests due to their high energy density, simple structure and ease of fuel storage and transportation. In DLFC, liquid fuel is fed to the anode where the oxidation reaction occurs, while air or oxygen is fed to the cathode for the reduction reaction. There are several types of DLFC such as direct methanol fuel cell (DMFC), direct ethanol fuel cell (DEFC) and direct formic acid fuel cell (DFAFC). The large-scale commercialization of these DLFCs is hindered by their major challenges such as fuel crossover and high cost of platinum (Pt) based catalyst used for oxygen reduction reaction (ORR) in the cathode. For this reasons, non-precious metal catalysts (NPMCs) are widely investigated as an alternative for the conventional Pt-based catalyst in DLFC application. Fe- and Co- nitrogen doped-carbon (NC) catalyst that was proved to exhibits high methanol tolerance and promising as the cathode catalyst for DMFC. From the single DMFC performance test reported in literatures, the better methanol tolerance and higher stability of the TM-NC catalysts as compared to Pt/C catalyst was also evidenced especially at higher operating temperature and higher methanol concentration. However, their power density is remains low as summarized in Table 1. Therefore, the aim of this study is to achieve high performance in DLFC by applying the TM-NC as cathode catalyst in direct formic acid fuel cell (DFAFC) operation. As the application of the TM-NC catalyst in DFAFC has not yet been studied, the fuel tolerance on the TM-NC catalyst in acidic and alkaline medium were determined in this study. Further, the single DFAFC performance test was conducted and the result achieved was compared with the DFAFC operation using conventional Pt/C cathode catalyst and the other DLFC operation reported in other studies.

Table 1 Comparison of single DMFC performance using Fe- or Co-N-C and Pt/C cathode catalyst

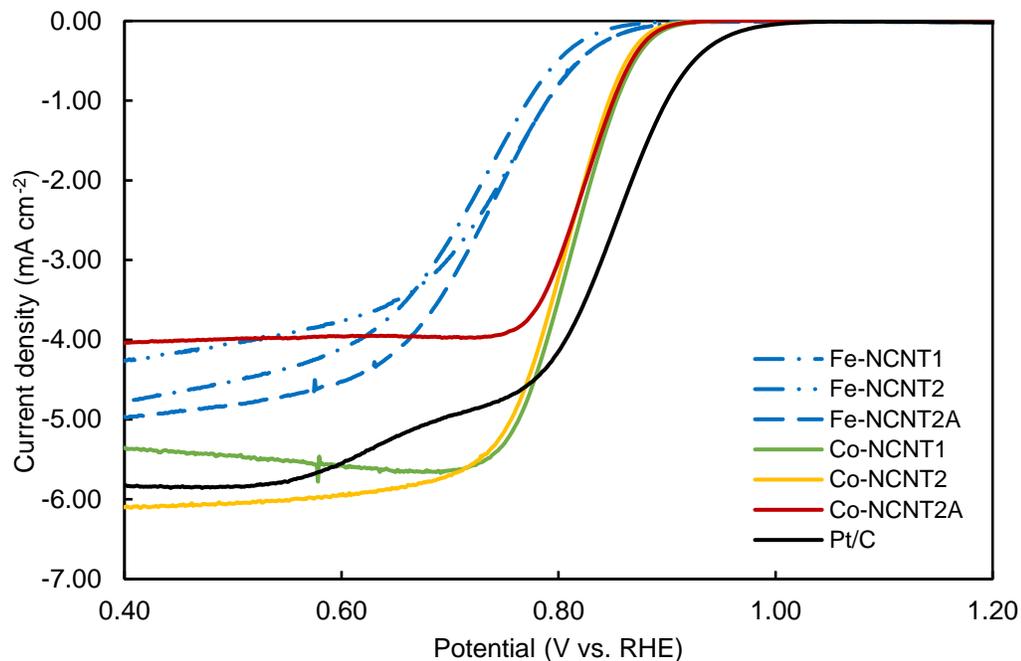
Reference	Operating temperature (°C)	Methanol concentration (M)	Oxygen flow rate	Cathode catalyst	Open circuit voltage (OCV)	Maximum power density (mW cm ⁻²)
D. Sebastian et al. 2016	90	5	100 ml min ⁻¹ (humidified)	Fe-NC Pt/C	0.75 ~0.60	35 65
D. Sebastian et al. 2017	90	5	100 ml min ⁻¹ (humidified)	Fe-NC Pt/C	- -	~62 ~60
D. Sebastian et al. 2017	90	10	100 ml min ⁻¹ (humidified)	Fe-NC Pt/C	0.82 0.50	60 ~42
D. Sebastian et al. 2017	110	17	100 ml min ⁻¹ (humidified)	Fe-NC Pt/C	0.78 0.45	58 26
Osmieri et al. 2017	90	2	200 Nml min ⁻¹ (dry)	Fe-NC Pt/C	0.70 0.60	19.6 30.9

The methodology for this study involves the catalyst preparation, physical and electrochemical characterization of the prepared catalyst and single cell performance measurement. Herein, Fe-NCNT and Co-NCNT were synthesized using the conventional method by pyrolysis of multi-walled carbon nanotubes, dicyandiamide, and metal salt in a N₂ atmosphere at 800°C for 2 h. X-ray diffraction (XRD) analysis and X-ray photoelectron spectroscopy (XPS) were used to determine the crystallite structure, elemental surface composition and nitrogen-carbon binding configuration in the catalyst prepared. Electrochemical measurement was done by using conventional three-electrode electrochemical cell to determine the ORR activity of the catalysts. Then, single cell performance test was conducted by using the TM-NC catalyst synthesized as the cathode catalyst in hydrogen-fed polymer electrolyte fuel cell (PEFC) and DFAFC operation, the electrochemical measurement and single cell testing were also carried out for the commercial Pt/C catalyst for comparison.

First, the effect of pyrolysis step and acid treatment of the catalysts on the ORR activity in acidic and alkaline medium are investigated. The ORR activity curves obtained from the electrochemical measurement in acidic and alkaline medium are shown in Figure 1. Different pyrolysis steps show different effect on ORR activity in acidic and alkaline medium. It was found that, Fe-NCNT catalyst is more active than Co-NCNT catalyst in acidic medium whereas Co-NCNT catalyst is more active in alkaline medium. Even though both catalysts showed lower ORR activity than that commercial Pt/C catalyst in, they exhibited higher formic acid and formate tolerance than the Pt/C catalyst in acidic and alkaline medium, respectively as shown in Figure 2 and Figure 3. The commercial Pt/C catalyst showed an oxidation peak in the presence of formic acid and formate indicates low tolerance toward the fuels. For durability test, Co-NCNT catalyst exhibited excellent stability in both acidic and alkaline medium whereas Fe-NCNT catalyst shows comparable stability with that commercial Pt/C catalyst.

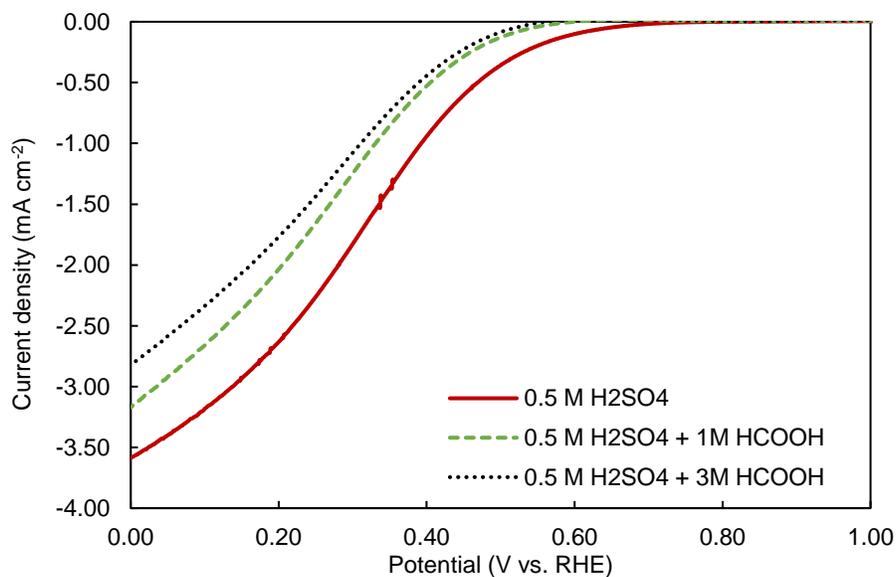


(a) Acidic medium

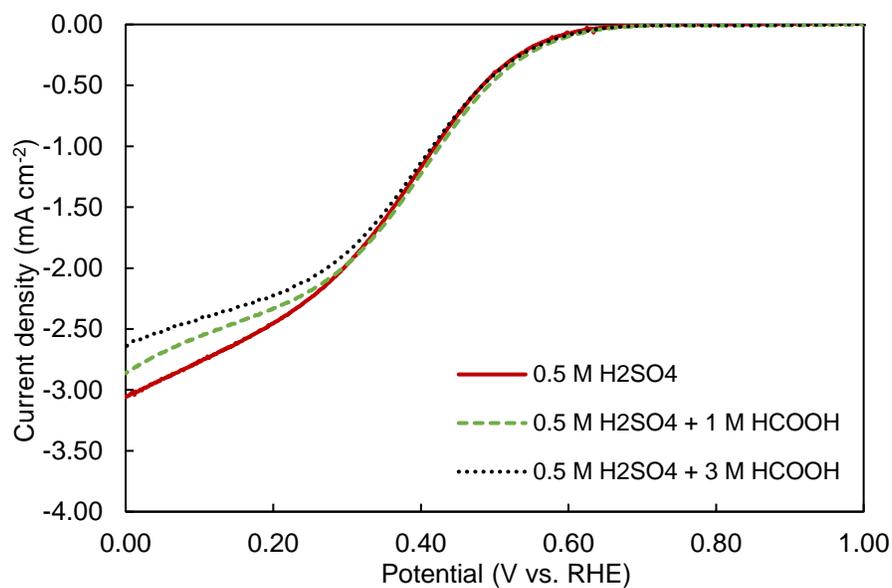


(b) Alkaline medium

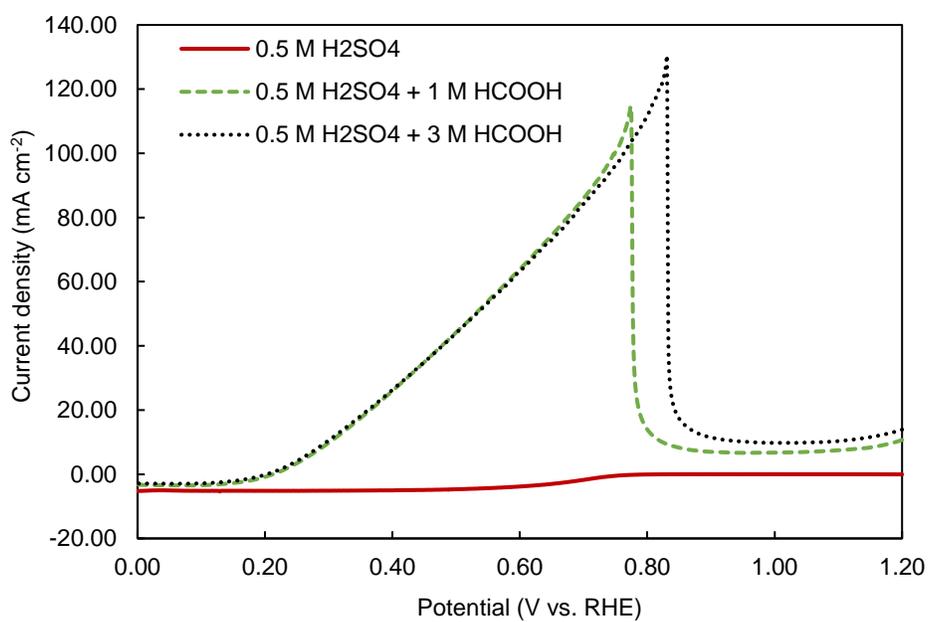
Figure 1 RDE polarization curve of ORR on Fe-NCNT, Co-NCNT and commercial Pt/C catalyst in (a) 0.5 M H₂SO₄ and (b) 0.1 M KOH at rotations rate of 1900 rpm and potential scan rate of 10 mVs⁻¹



(a) Fe-NCNT1

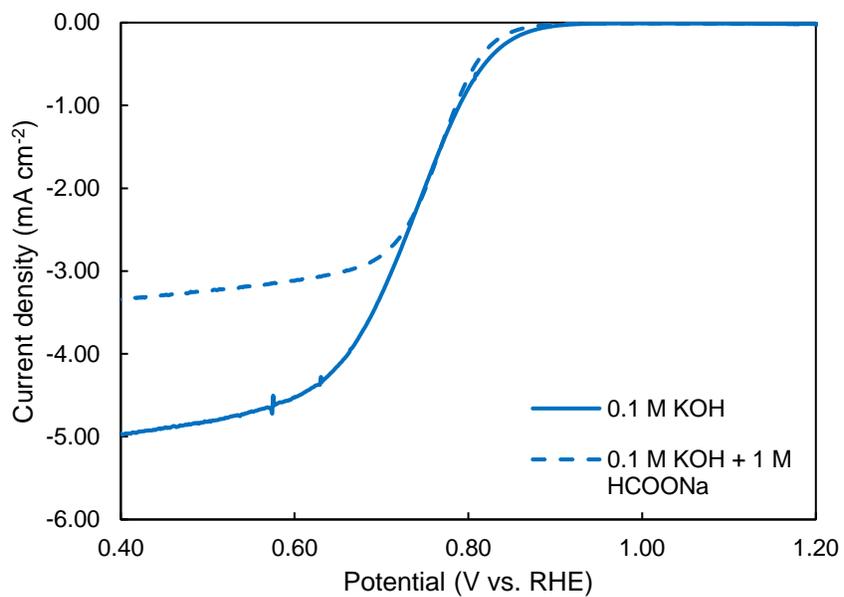


(b) Co-NCNT1

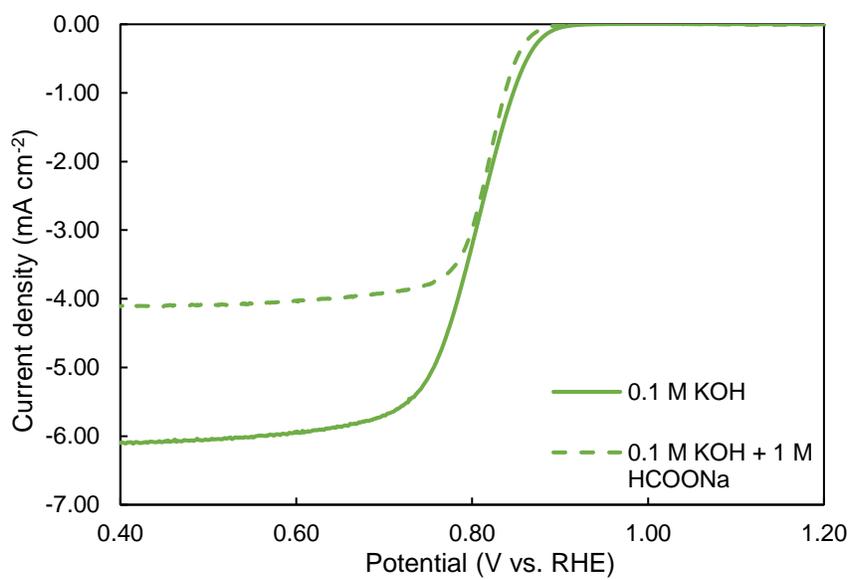


(c) Pt/C

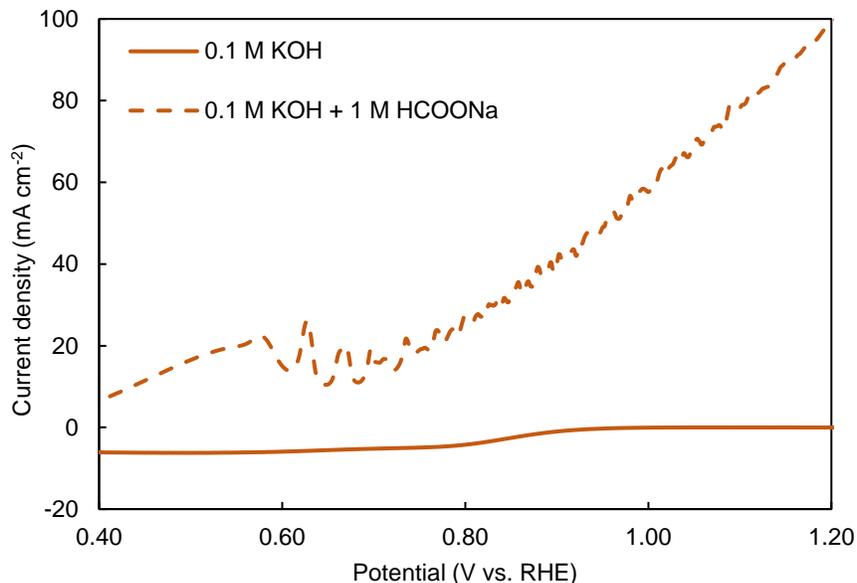
Figure 2 ORR activity curve for (a) Fe-NCNT1 (b) Co-NCNT1 and (c) Pt/C catalyst (50 wt. %) in O₂-saturated 0.5 M H₂SO₄ with and without formic acid (HCOOH) at rotation rate of 1900 rpm



(a) Fe-NCNT2A



(b) Co-NCNT2

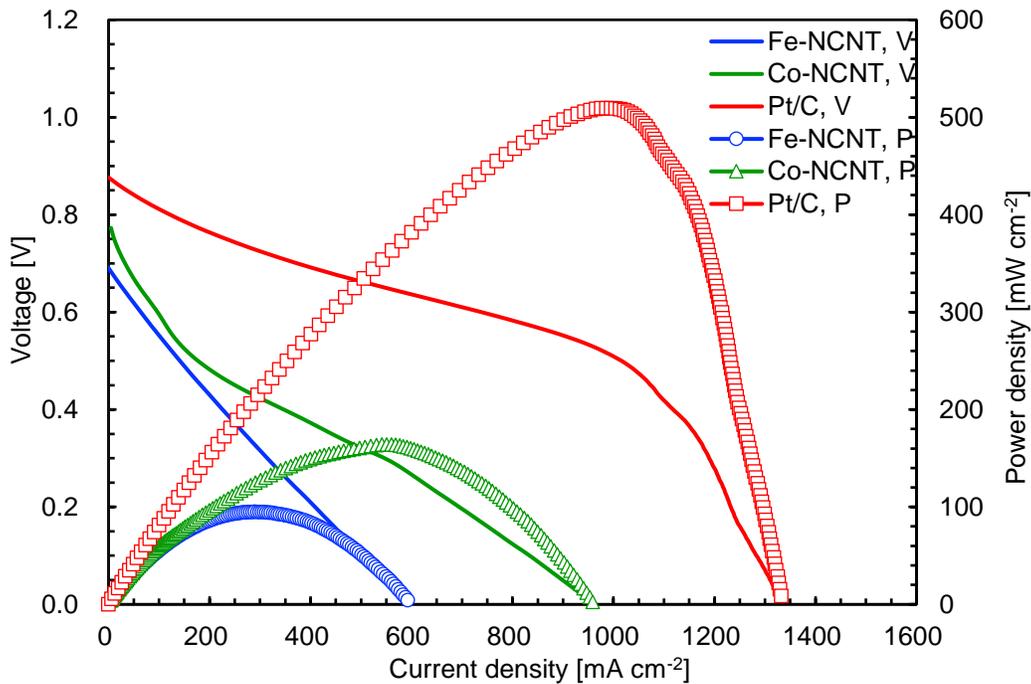


(c) Pt/C

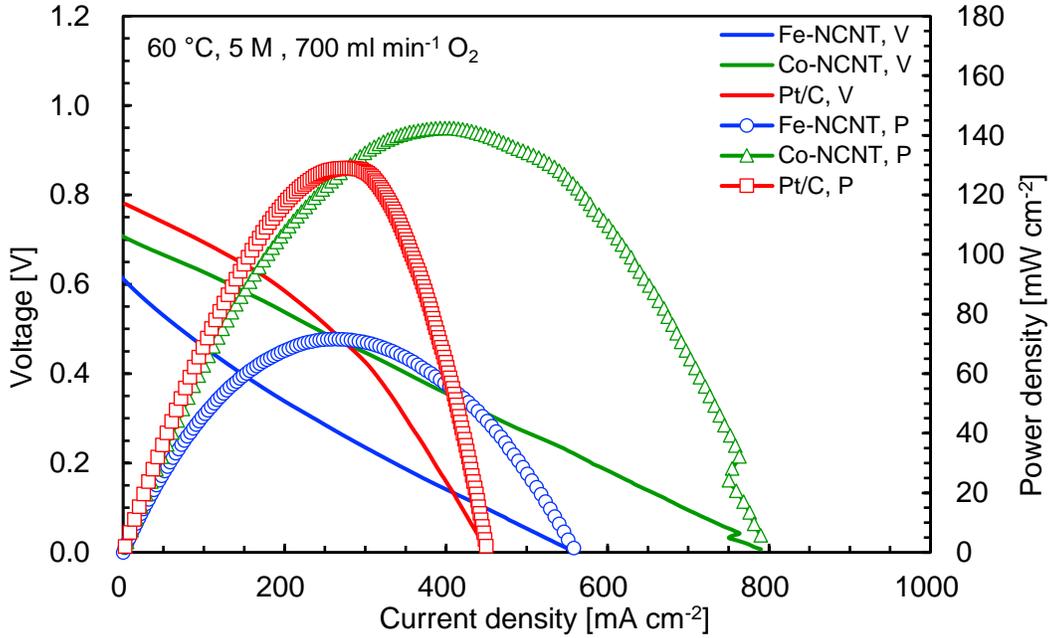
Figure 3 ORR activity curve for (a) Fe–NCNT2A, (b) Co–NCNT2 and (c) commercial Pt/C catalyst (50 wt. %) in O₂-saturated 0.1 M KOH with and without sodium formate (HCOONa) at rotation rate of 1900 rpm

Next, the Fe–NCNT and Co–NCNT catalysts that exhibited highest ORR activity were applied to the cathode DFAFC and the single cell performance test was conducted. Single cell tests with hydrogen–oxygen (PEFC) and DFAFC operations were conducted under various operating conditions to compare the performance of the cells using the prepared catalysts and the conventional Pt/C catalyst. From the polarization and power density curves result in PEFC operation as shown in Figure 4 (a), the performances of PEFC with both Fe–NCNT and Co–NCNT catalysts were significantly lower than Pt/C catalyst, 94.9 mW cm⁻² for Fe–NCNT and 164.0 mW cm⁻² for Co–NCNT at 60°C.

Nevertheless, the Co-NCNT catalyst showed the maximum power density of 142.4 mW cm⁻² in DFAFC operation at 60 °C and 5 M formic acid. This value is the highest as compared with the Fe-NCNT and Pt/C catalyst as shown in Figure 4 (b). The DFAFC operation using Co-NCNT as the cathode catalyst was further tested at different operating condition to find the optimum operating condition. The performance was measured at 30 °C and 60 °C operating temperature, with formic acid concentration from 3 M to 10 M and different oxygen flow rates (300, 500 and 700 ml min⁻¹). The maximum power density achieved was summarized in Figure 5. It was observed that the optimum operating condition for DFAFC using the Co-NCNT as the cathode catalyst is at 60 °C operating temperature, 7 M formic acid and 700 ml min⁻¹ oxygen flow rate with maximum power density of 160.7 mW cm⁻².



(a) PEFC operation



(b) DFAFC operation

Figure 4 Polarization curve and power density curve for the (a) PEFC and (b) DFAFC operation using Fe-NCNT, Co-NCNT, and commercial Pt/C as the cathode catalysts at 60°C operating temperature

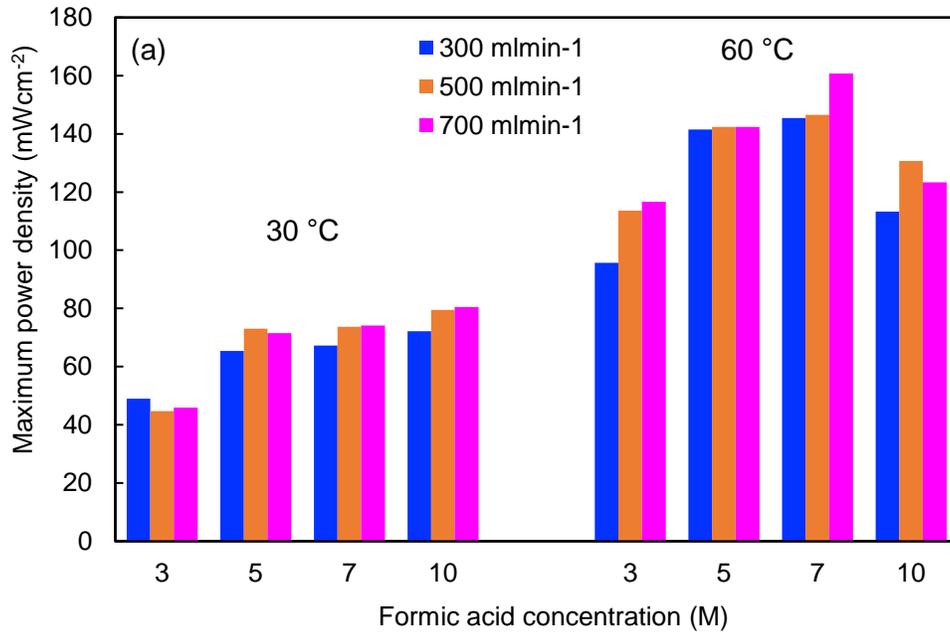


Figure 5 Maximum power density as a function of formic acid concentration at 30°C and 60°C operating temperatures and different oxygen flow rates in DFAFC operation

The performance result obtained in this study was compared with the other studies done in DLFC, particularly DMFC as summarized in Table 2. It was found that the maximum power density achieved in this study is the highest as compare to the other reported studies using Fe- and Co-NC for the cathode catalyst. It can be concluded that, the Fe-NCNT and Co-NCNT catalysts used in this study showed high performance in the DFAFC operation and thus, high performance in DLFC operation achieved in this study. However, it is necessary to further optimize the other MEA fabrication parameters such as the catalyst loading and ionomer loading on the cell performance in future work. The performance of single direct formate fuel cell (DFFC) using those catalysts at the cathode also should be measured as they show good ORR activity and fuel tolerance in alkaline medium.

Table 2 Summary of performance for DMFC with Fe- and Co-based catalysts at the cathode

Operation	Cathode catalyst	Open circuit voltage (V)	Max. power density (mWcm ⁻²)	Feed concentration (M)	Oxygen/ air	Operating temperature (°C)	Reference
DMFC	Fe-NCB 4 mg cm ⁻²	0.82	60	10	Humidified oxygen 100 ml min ⁻¹	90	Sebastian et al. 2017
DMFC	Fe-NCNT 2.5 mg cm ⁻²	0.57	7.7	2	Dry oxygen 200 Nml min ⁻¹ 3 bar backpressure	90	Osmieri et al. 2017
DMFC	Fe-NMPC 2.5 mg cm ⁻²	0.64	22.6	2	Dry oxygen 200 Nml min ⁻¹ 3 bar backpressure	90	Osmieri et al. 2017
DMFC	Co-NC 10 mg cm ⁻²	~0.50	53.2	2	Oxygen 100 ml min ⁻¹	60	Y. Wei 2012
DFAFC	Fe-NCNT 4.6 mg cm ⁻²	0.63	71.5	5	Dry Oxygen 500 ml min ⁻¹	60	This study
DFAFC	Co-NCNT 3.3 mg cm ⁻²	0.70	160.7	7	Dry oxygen 700 ml min ⁻¹	60	This study

学位論文審査報告書（甲）

1. 学位論文題目（外国語の場合は和訳を付けること。）

Study on the non-precious metal catalyst for cathode in a direct formic acid fuel cell

（直接ギ酸形燃料電池のカソード用非貴金属触媒に関する研究）

2. 論文提出者 (1) 所 属 機械科学 専攻

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3. 審査結果の要旨（600～650字）

当該学位論文に関し、令和元年8月2日に第1回学位論文審査委員会を開催し、提出された学位論文および関係資料について詳細に検討した。さらに、同日に行われた口頭発表後に第2回学位論文審査委員会を開き、協議の結果、以下のように判定した。

直接ギ酸形燃料電池(DFAFC)は近年注目を集めているが、電極触媒に貴金属を大量に使用することが実用化の妨げの一因となっている。特にカソードに用いるPtは、酸素還元反応活性は高いものの、アノードから透過した未反応ギ酸の酸化に対しても高い活性を示す。これにより、DFAFCの性能は未だに低い。そこで本研究では、非貴金属かつギ酸の酸化活性が低いカソード触媒として、窒素とFeまたはCoを導入したカーボンナノチューブ(Fe, Co-NCNT)に注目し、これらのDFAFCへの適用可能性を検討した。まず異なる条件でこれらを合成し、(1)いずれの触媒もギ酸が混入しても酸素還元活性がほとんど低下しないことを明らかにした。(2)この結果に基づき、作製したDFAFCでは、Co-NCNTを用いた際に60℃で160 mW/cm²を凌ぐ活性が得られ、Ptを用いた従来のDFAFCよりも高い出力が得られることを明らかにした。これらの成果に対する関連産業界・学界からの注目度は高く、今回提案した代替触媒をDFAFCに適用することで、DFAFCの実用化の促進も期待されるため、工学的価値が高いと判定し、博士(工学)に値するものと判定した。

4. 審査結果 (1) 判定 (いずれかに○印) 合格 不合格

(2) 授与学位 博士(工学)