

IN-SITU CO₂ CURRENT EFFICIENCY MEASUREMENT OF DIRECT ETHANOL FUEL CELL

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ABSTRACT

In this present work, we carry out systematically study on catalyst for ethanol electrooxidation in direct ethanol fuel cell. For cathode catalyst we use a commercial catalyst of 40% Pt/C from ETEK. Catalysts were printed on to carbon paper of TGPH 060 and sandwiched into membrane electrode assembly (MEA) and then arranged in fuel cell with the geometric area 1.2 cm². As an electrolyte, we used Nafion 117 from Du Pont. On-line Differential Electrochemical Mass Spectrometry (DEMS) measurement in fuel cell setup was carried out in order to determine the activity and selectivity which was indicated by result of Faradaic current and CO₂ current efficiency of ethanol electro-oxidation respectively. PtRhCeO₂/C was significantly improve the selectivity to form of CO₂ in comparison to the commercial catalyst of 20% Pt/C from Alfa Aesar- Johnson Mattews . Increasing of selectivity is shown by increase of CO₂ current efficiency of ethanol oxidation of about 25 percent in comparison to references catalyst of 20% Pt/C Alfa Aesar-JM

Key words: Membrane electrode assembly (MEA), DEMS, ethanol electro-oxidation

ABSTRAK

Pada penelitian ini dilakukan kajian sistematis terhadap katalis 20% PtRhCeO₂/C pada *fuel cell* dengan bahan bakar *ethanol*. Pada sisi katoda digunakan katalis komersial 40% Pt/C dari ETEK. Katalis tersebut di cetak pada kertas karbon TGPH 060 dan dirangkai dalam *membrane electrode assembly* (MEA) kemudian pasang dalam *fuel cell* dengan luasan geometrik 1,2 cm². Sebagai elektrolit digunakan Nafion 117 dari Du Pont. Pengukuran secara on-line dengan *Differential Electrochemical Mass Spectrometry* (DEMS) dilakukan untuk mengetahui aktivitas dan selektivitas katalis yang ditunjukkan dengan arus Faraday dan efisiensi arus CO₂ dari reaksi elektrooksidasi yang terjadi. Katalis PtRhCeO₂/C terbukti meningkatkan selektivitas katalis menuju pembentukan CO₂ dibandingkan dengan katalis komersial 20% Pt/C Alfa Aesar-Johnson Mattews. Peningkatan selektivitas ditunjukkan dengan kenaikan efisiensi arus CO₂ pada elektro-oksidasi *ethanol* sebesar 25% dibanding dengan katalis rujukan 20% Pt/C Alfa Aesar-JM

Kata kunci: *Membrane electrode assembly* (MEA), DEMS, Elektro-oksidasi *ethanol*

1. INTRODUCTION

Direct oxidation fuel cell (DOFC) is one candidate for application in vehicle and portable power. The advantage of DOFC is that additional equipment like fuel reformer is not necessary. Alcohol and mainly methanol are widely proposed as possible fuel for direct methanol fuel cell (DMFC). One of the main advantages of methanol is its availability, its low price and the easiness of its storage as a liquid. However, there is a problem that methanol is toxic for human. Based on these aspects of DMFC, there are several kinds of

fuels which are investigated as a fuel of direct type fuel cell. Ethanol is one of them. It is well known that ethanol is not toxic for human and is easily produced from biomass. This means that carbon dioxide (CO₂) emitted from direct type fuel cell using ethanol as a fuel can be recycled by planting. Ethanol as alternative fuel for direct ethanol fuel cell (DEFC) also has a relative high energy density (8 kWh/kg) and for comparison methanol energy density was 6 kWh/kg.

The case of oxidation of ethanol is more complicated than methanol which is necessary to break C-C bond to obtain the total oxidation reaction. To obtain this, it is necessary to modify the structure or composition of anode catalyst. Electrocatalytic oxidation of ethanol using platinum or platinum alloy catalyst has been investigated [1-3], and the products formed by the electrocatalytic oxidation of ethanol and the oxidation reactivity of ethanol were discussed from many aspects. Iwasita and Pastor studied the adsorb behavior of ethanol on a polycrystalline platinum using a differential electrochemical mass spectroscopy (DEMS) and FTIR [1]. They reported many adsorbed species formed by the oxidation of ethanol and observed the evolution of CO₂. The aim of the present paper is to investigate the activity and selectivity of the PtRhCeO₂/C catalyst for electrooxidation of ethanol. The result was compared to the commercial Pt/C catalyst from Alfa Aesar-Johnson Matthews.

2. EXPERIMENT

2.1. Membrane Electrode Assembly (MEA)

In this experiment we used 20% PtRhCeO₂/C catalyst (prepared at Technical University of Munich) as anode catalyst and 20% Pt/C (Alfa Aesar - Johnson Matthew) as reference catalyst. As cathode catalyst is used 40% Pt/C (from ETEK). Catalyst ink was prepared by mixing the required amount of catalyst powder with 20 % Nafion® solution (Du Pont) to give 30% wt. of Nafion, and then diluted with a mixture of millipore™ water and 2-propanol. The resulting ink then placed in an ultrasonic bath for 10 minutes or until the catalyst powder had fully dispersed. This ink then sprayed onto a piece of carbon Toray paper TGPH 060 which was kept at 110°C throughout the process, in order to assist the binding of the catalyst to the backing layer. The spraying machine consisted of motorised X-Y table controlled by a CNC automation controller. The catalyst layer on carbon paper then sandwiched into carbon paper to make-the membrane electrode assembly (MEA)

2.2. Description of DEMS Setup

The DEMS setup which consisted of two differentially pumped chambers, a Balzers QMS 200 mass spectrometer, AGEF potentiostat and computerized data acquisition system. The DEMS sensor was located at the outlet channel of anode compartment, it consist of a cylindrical detection volume with a diameter of 7 mm and a height of 2 mm through which

anode outlet flow passes. This volume is separated from the vacuum system of the mass spectrometer by a Micro porous Teflon membrane (Schleicher & Schuell, TE-30) with a pore size of 0.02 micrometer and a thickness of 110 micrometer. The membrane is supported by a Teflon disc of 2 mm in diameter, with holes.

The fuel cell consisted of two stainless steel plates with integrated serpentine medium distribution channels. Six threaded studs and nuts held the two plates together. The fuel cell can be operated in both modes half-cell and full cell. Generally during the investigation of anode it is used as a half-cell. Cathode with Pt loading ($2.5\text{mg}/\text{cm}^2$) and continuous hydrogen flow works as counter and reference both. Potential of the cathode is assumed to be same as of the reversible-hydrogen electrode (RHE). All potential are reported in reference to this. Schematic diagram of DEMS setup is shown in Fig.1.

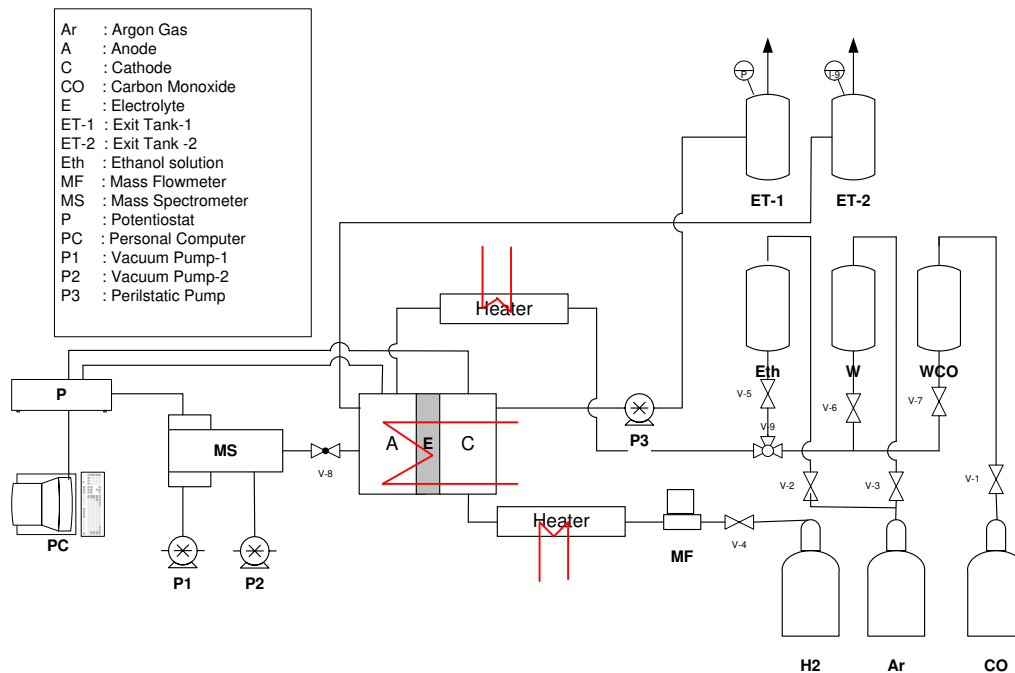


Fig. 1. Schematic diagram of DEMS setup

2.3. Calibration of DEMS System

The main products of ethanol electrooxidation are carbon dioxide, acetaldehyde and acetic acid. From those three products, they were only carbon dioxide and acetaldehyde that can be monitored by DEMS measurement because its high volatility. The main problem in

DEMS measurement is because the mass number of both CO₂ and CH₃CHO is the same at 44 and to monitor both together is not possible at m/z= 44. To solve this problem, Fujiwara et al.[4],used deuterated ethanol (CD₃CH₂OH) for determining reaction products that had same mass number. Due to the high cost of this material, extensive utilization is limited. To avoid interference between CO₂⁺ and CH₃CHO⁺ ion current (both at m/z =44), which are the major ethanol electrooxidation products, carbon dioxide and acetaldehyde was monitored at m/z =22 and m/z =29 respectively. The calibration of DEMS for CO₂ is performed with H₂ oxidation current interference and potentiostatic bulk CO oxidation.

2.4. In-situ DEMS Measurement

Potentiodynamic Measurements: Cyclic Voltammogram and Mass Cyclic Voltammogram for ion currents m/z =22, 29, 15 and 30 from 0 – 1.0 V vs RHE with scanrate 5 mV/s at temperature 90°C. Steady state voltammogram for ethanol electrooxidation was recorded after several cycles.

Potentiostatic DEMS Measurements: monitoring transient faradaic current and ion mass current by stepping the potential from 0 V vs RHE to 0.5, 0.6, 0.7 ,and 0.8 V vs RHE (10 minutes for each potential step), with scanrate 5 mV/s at temperature 90°C for Cyclic Voltammogram and Mass Cyclic Cyclic Voltammogram for ion currents m/z =22, 29, 15 and 30.

3. RESULT AND DISCUSSION

3.1. Potentiodynamic Measurement

Figure 2 and Fig. 3 show the CV and MSCV for PtRhCeO₂/C and Pt/C catalyst respectively as function of cell potential by potentiodynamics measurement technique. These figures comprise of cyclic voltammogram (CV) /Faradaic current, and the mass spectrometric cyclic voltammogram (MSCV) for ion currents m/z =22, m/z=29, m/z= 15, and m/z=30.

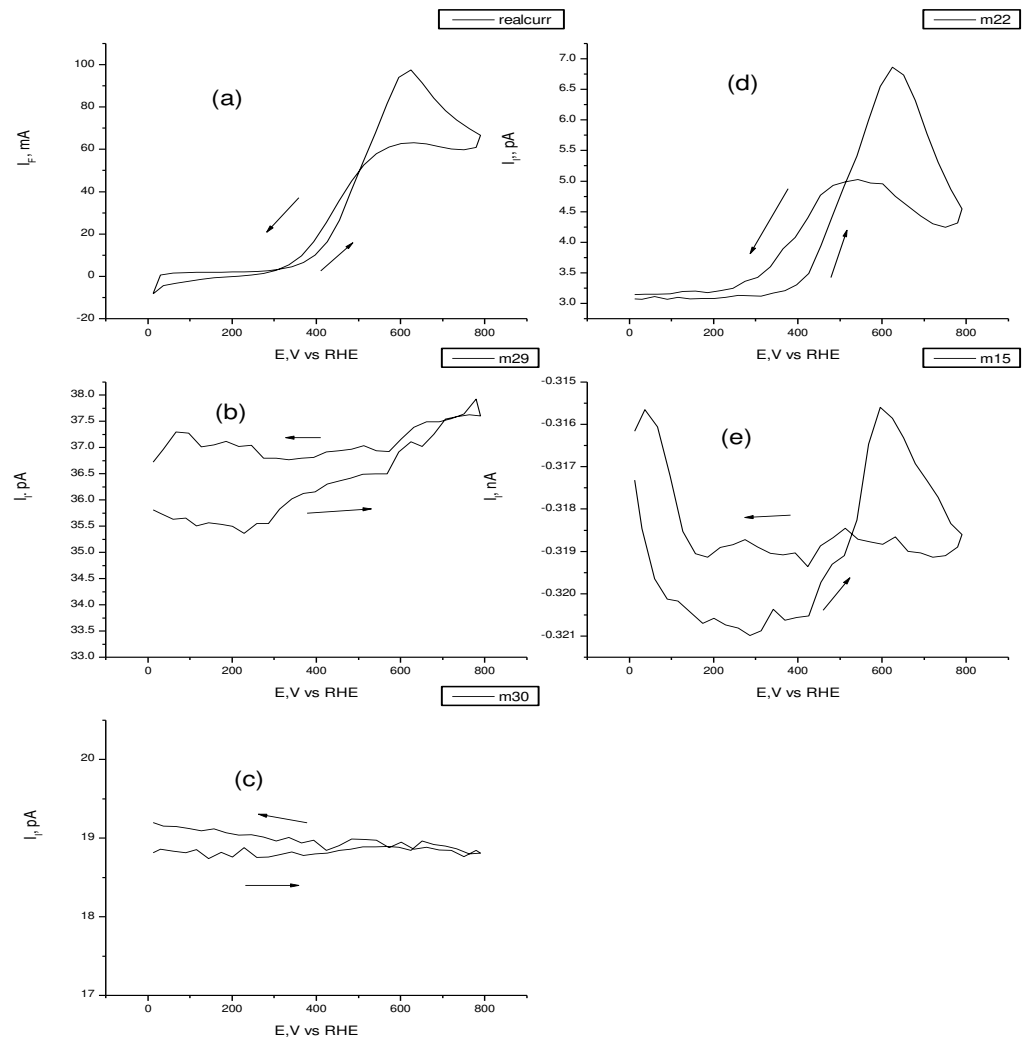


Fig. 2. CV and MSCV of 20% PtRhCeO₂/C catalyst at temperature 90°C, ethanol flowrate 5 ml/min, with scanrate 5 mV/s(a) CV (b) MSCV for m/z = 29 (c) MSCV for m/z = 30 (d) MSCV for m/z = 22 and (e) mSCV for m/z = 15

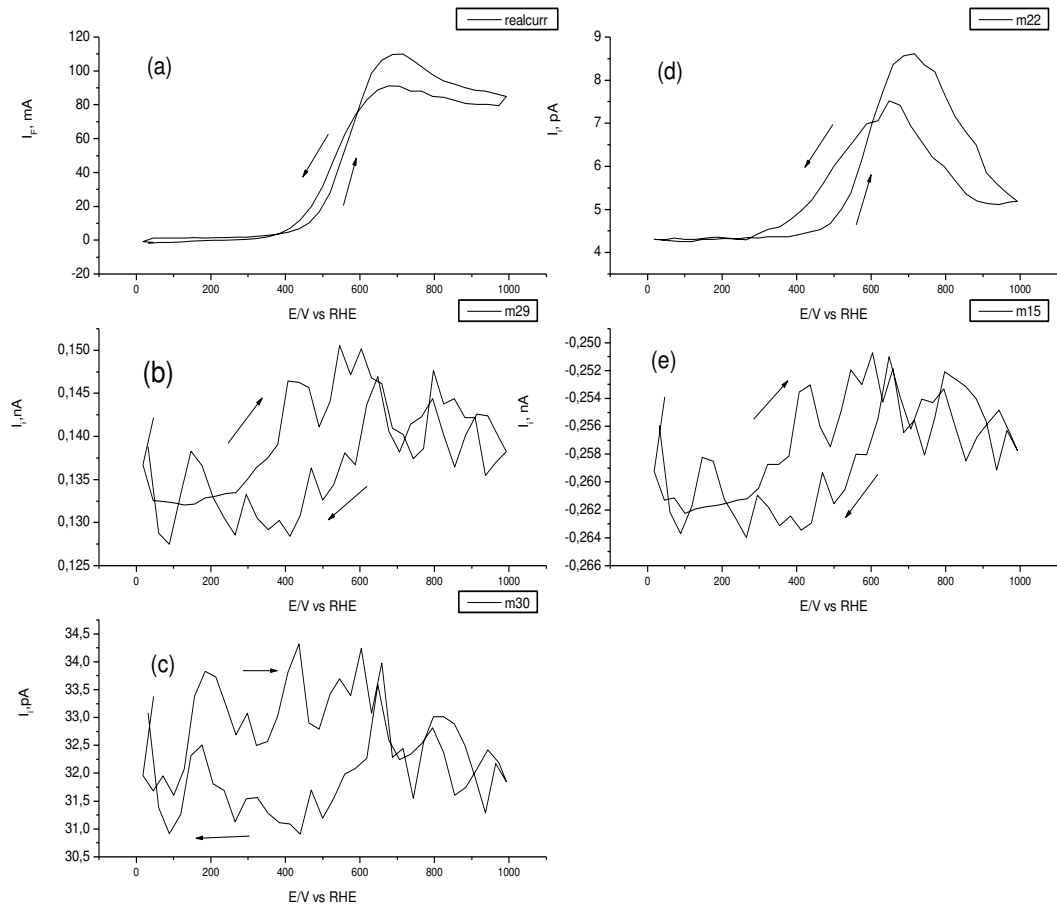


Fig. 3. CV and MSCV of 20% Pt/C catalyst at temperature 90°C, ethanol flowrate 5 ml/min, with scanrate 5 mV/s(a) CV (b) MSCV for $m/z = 29$ (c) MSCV for $m/z = 30$ (d) MSCV for $m/z = 22$ and (e) mSCV for $m/z = 15$

Ion current $m/z=22$ was corresponding to mass spectrometric signal for CO₂ via the doubly ionized molecular ion signal. The onset of CO₂ formation in the positive going scan of the steady state voltammogram occurred at ca.0.47 V vs. RHE for 20% Pt/C catalyst, while for catalyst 20% PtRhCeO₂/C the onset of CO₂ formation occurred at ca. 0.39 V vs. RHE. The CO₂ formation at rather high potential can be explained because of electrooxidation of ethanol at potential below ca.0.4V is largely blocked by adsorbed poisoning intermediates CO and hydrocarbon residues. This result was in agreement with reported by Wang et al [5]

3.2. Potentiostatic Measurement

Figure 4 shows the Faradaic current vs potential for different catalysts. Testing performance in DEMS is conducted at temperature 90 °C , 5 ml/minute ethanol flowrate, and with scanrate of 5 mV/s by potentiostatic measurements. This result indicated that Faradaic current of catalysts which added ceria provided higher current at low potential (up to 0.6 V) in comparison to Pt/C (Alfa Aesar-JM) catalyst reference. This means that by adding ceria on Pt-based catalyst could increase an activity of the catalysts at low potential, although this elevated in Faradaic current was not so high. In application of fuel cell, increase of Faradaic current at low potential is more useful compared to increase of Faradaic current at high potential. Therefore we want to further investigate increase of Faradaic current at the lower potential by analyzing of ion mass number 22 as shown in Fig.5

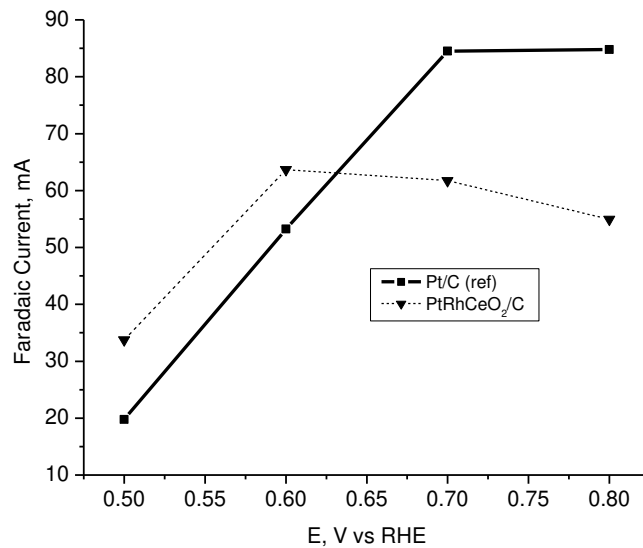
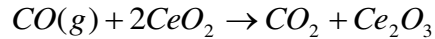


Fig. 4. Faradaic current vs. potential, at temperature 90°C, scanrate 5 mV/s, anode catalyst loading 0.8 mg/cm² for 20% PtRhCeO₂/C (dashed line) and 20% Pt/C Alfa Aesar-JM (solid line), cathode catalyst loading 2.5 mg/cm² (20% Pt/C ETEK)

Figure 5 shows relation between CO₂ current efficiency (CCE) versus potential. From this picture can be seen that an increase of Faradaic current which was occurred at low potential followed with increase significantly of CCE. 20% Pt/C (alfa aesar-JM) as our reference catalyst provide lower performance than ceria added catalysts, especially at low potential (< 0.6 V). By increase of the CO₂ current efficiency, indicated that oxidation reaction was occurred at a total oxidation reaction or mostly happen the C-C bond breaking of ethanol. It was because mostly CO₂ product was resulted from oxidation of CO_{ads} species of ethanol. These increases in CO₂ current efficiency (CCE) may effect of ceria addition in the

catalyst. The role of ceria in the oxidation of carbon monoxide was agreed to what reported by Thi sayle *et al.* [6] :



Where oxygen was extracted from an exposed surfaces of the CeO₂, facilitated by reduction of Ce⁴⁺ to Ce³⁺.

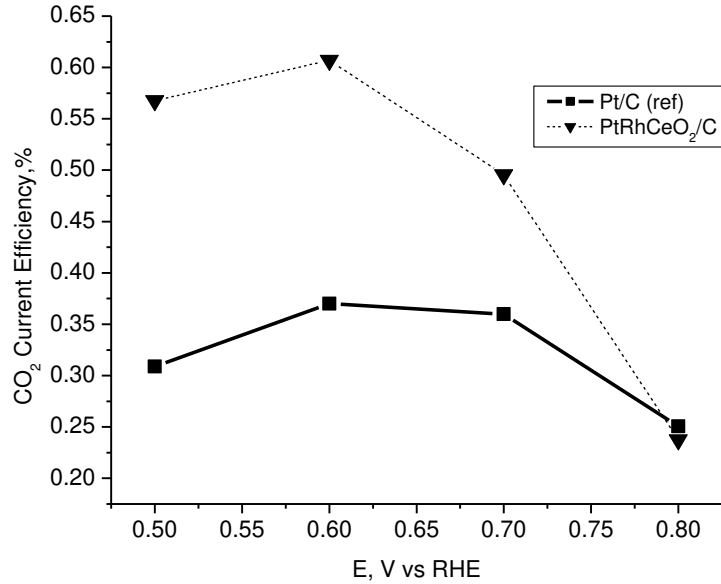


Fig. 5. CO₂ current efficiency vs. potential, at temperature 90°C, scanrate 5 mV/s, anode catalyst loading 0.8 mg/cm² for 20% PtRhCeO₂/C (dashed line) and 20% Pt/C Alfa Aesar-JM (solid line), cathode catalyst loading 2.5 mg/cm² (20% Pt/C ETEK)

Figure 6 represents the correlation between CCE to the platinum loading of catalysts. Comparing of 20% PtRhCeO₂/C catalyst to the 20% Pt/C commercial catalyst with almost no difference in platinum loading (PtRhCeO₂/C = 0.92 mg/cm² and Pt/C =0.845 mg/cm²) provided significant improvement value of CCE. Increasing of the CCE over PtCeO₂ catalyst at equal of catalyst loading will reduce cost of catalyst in fuel cell application.

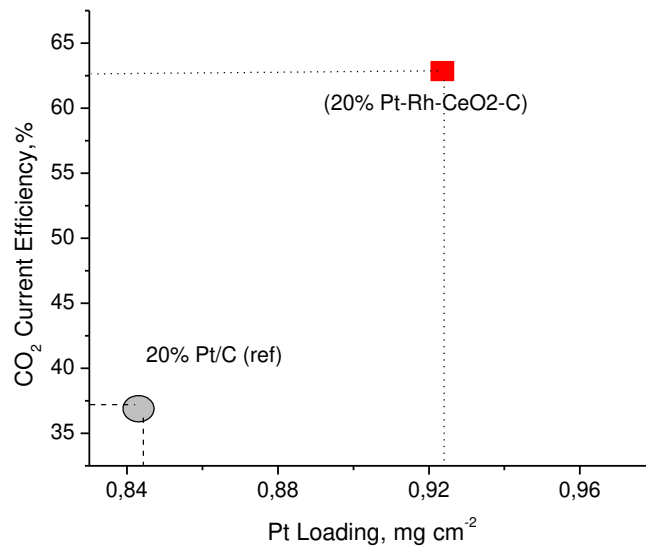


Fig. 6. CO₂ current efficiency vs CO stripping charge for different catalysts at potential 0.6 V, temperature 90^oC, scan rate 5 mV/s, ethanol flowrate 5 ml/min

4. CONCLUSION

The product of the ethanol oxidation reaction over Pt/C and PtRhCeO₂/C catalysts which investigated by in-situ DEMS were CO₂, Acetaldehyde, methane, ethane, while acetic acid couldn't detect by DEMS due to its low volatility.

Performance comparison of DEMS measurement result between 20% PtRhCeO₂/C and 20% Pt/C catalyst indicated that over PtRhCeO₂/C catalyst provided higher activity than Pt/C which is indicated by increase on Faradaic current and provided higher selectivity of the catalysts which is indicated by increasing of CO₂ current efficiency. Both increase of activity and selectivity were occurred at low potential (≤ 0.6 V). Improvement of CO₂ current efficiency of ethanol oxidation was about 25 % in comparison to references catalyst of 20% Pt/C Alfa Aesar-JM

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