Development of Pt-CeO2/C and Pt-Rh-CeO2/C catalysts for ethanol electro-oxidation in direct ethanol fuel cell = Pengembangan katalis PtCeO2/C dan PtRhO2/C untuk elektro-oksidari ethanol pada direct ethanol fuel cell

Hariyanto, author

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Abstrak

Direct oxidation fuel cells (DOFCs) telah banyak menarik perhatian sebagai alternative pengganti dari hydrogen-fuel cell dikarenakan lebih mudah penanganan dan transportasi bahan bakarnya. Penggunaan bahan bakar cair pada DOFC akan lebih sederhana dibandingkan hydrogen dan tidak memerlukan infrastruktur baru pada trasnportasi bahan bakarnya. Ethanol adalah salah satu kandidat bahan bakar untuk DOFC yang mempunyai kelebihan diantaranya : tidak beracun, sebagai bahan bakar terbaharukan, dan mempunyai kerapatan energi yang tinggi. Akan tetapi penggunaan ethanol pada direct ethanol fuel cell (DEFC) dihadapkan pada permasalahan utama yaitu kesulitan untuk memutus ikatan C-C pada ethanol dimana reaksi oksidasi akan terjadi secara parsial sehingga energi listrik yang dihasilkan tidak maksimal . Untuk memecahkan masalah tersebut maka penelitian ini bertujuan untuk mengembangkan katalis anoda berbasiskan platina berpenyangga karbon untuk oksidasi ethanol yang mampu memutus ikatan C-C menuju reaksi oksidasi total. Tujuan khusus yang pertama pada penelitian ini adalah studi pengaruh penambahan rhodium pada katalis platina berpenyangga karbon terhadap aktivitas dan selektivitas katalis untuk oksidasi ethanol. Tujuan khusus kedua adalah studi pengaruh penambahan ceria pada katalis platina berpenyangga karbon terhadap aktivitas dan selektivitas katalis untuk oksidasi ethanol. Sedangkan tujuan khusus ketiga adalah studi pengaruh penambahan rhodium dan ceria bersama-sama pada katalis platina berpenyangga karbon terhadap aktivitas dan selektivitas katalis untuk oksidasi ethanol. Metoda penelitian terdiri dari beberapa aktivitas yaitu: sintesis katalis, karakterisasi fisik katalis, karakterisasi elektrokimia, perakitan membrane electrode assembly (MEA), pengukuran on-line dengan teknik differential electrochemical mass spectrommtery (DEMS) dan uji kinerja fuel cell susunan tunggal. Ceria disintesis menggunakan teknik precipitasi konvensional dengan dua tahap. Sebagai pembanding pada penelitian ini juga digunakan ceria komersial dari Alfa Aesar. Preparasi katalis (Pt-CeO2/C, Pt-Rh/C and Pt-Rh-CeO2/C) dilakukan dengan teknik koloid menggunakan ethylene glycol sebagai reduktan. Semua katalis di preparasi dengan target 20% berat platinum. Katalis yang telah di preparasi kemudian di karakterisasi dengan SEM-EDX untuk menganalisa morphologi permukaan katalis, dengan XRD untuk menganalisa kristalinitas dan struktur katalis, dan transmission elektron mikroskopy (TEM) untuk mengukur diameter partikel dan distribusinya. Dari hasil karakterisasi fisik diketahui bahawa ceria yang disintesa adalah berbentuk kristal sama dengan ceria komersial dengan diameter kristal 9 nm, sedangkan diameter ceria komersial adalah 19 nm. Ukuran diameter partikel katalis Pt-CeO2/C and Pt-Rh-CeO2/C adalah sekitar 2-3.5 nm dan terdistribusi merata dengan sedikit agglomerasi. Dari hasil EDX diketahui bahwa semua elemen katalis terdeteksi. Karakterisasi elektrokimia dilakukan dengan normal cyclic voltammetry, chronoamperommetry, and cyclic voltammetry pada media asam dan basa. Karakterisasi elektrokimia dilakukan untuk menginvestigasi aktivitas katalis yang dinyatakan dengan arus faraday yang dihasilkan pada uji setengah sel. Uji DEMS dilakukan untuk investigasi aktivitas katalis dan selektivitas pembentukan CO2 yang telah dirakit dalam susunan fuel cell.

Katalis PtCeO2/C dan PtRhCeO2/C yang disintesis dengan metoda koloid meningkatkan aktivitas dan selektivitas terhadap pembentukan CO2 pada elektrooksidasi ethanol yang mengarah kepada reaksi oksidasi total pada pengujian di direct ethanol fuel cell (DEFC). Penambahan rhodium (Rh) pada katalis Pt/C meningkatkan kemampuan untuk memutus ikatan C-C pada ethanol. Akan tetapi hasil pemutusan ikatan C-C tersebut tidak semua di konversi menjadi CO2 di sebabkan adsorpsi CO pada permukaan Rh yang kuat, sehingga peningkatan activitas dan selektivitas katalis tersebut tidak terlalu besar. Penambahan CeO2 pada katalis Pt/C meningkatkan kemampuan katalis untuk memutus ikatan C-C pada elektro-oksidasi ethanol, sekaligus meningkatkan kemampuan katalis untuk mengoksidasi lanjut CO intermediate product menjadi CO2. Peningkatan aktivitas dan selektivitas katalis tersebut disebabkan fungsi CeO2 sebagai pendonor oksigen kepada permukaan platina, sehingga dengan adanya oksigen yang cukup pada permukaan platina meningkatkan kemampuan memutus ikatan C-C dan meningkatkan kemampuan mengkonversi CO menjadi CO2. Penambahan Rh dan CeO2 secara bersama-sama meningkatkan activitas dan selektivitas katalis pada reaksi elektro-oksidasi ethanol. Peningkatan tersebut lebih besar dibandingkan jika hanya di tambah rhodium saja ataupun hanya ditambahkan CeO2 saja. Penambahan keduanya tersebut akan bersinergi sehingga meningkatkan aktivitas dan selektivitas katalis PtRhCeO2/C. Peningkatan aktivitas katalis yang disintesis (in-house) terhadap katalis referensi Pt/C pada potential 0,6 V dan suhu operasi 90oC adalah : 20% PtCeO2/C (in-house CeO2): 5.99%, 20% PtCeO2/C (commercial CeO2): 3.89%, 20% PtRhCeO2/C (in-house CeO2): 19.6%, 20% PtRhCeO2/C (Commercial CeO2): 26.3%. Peningkatan selektivitas katalis yang di sintesis (in-house) untuk pembentukan CO2 terhadap katalis referensi Pt/C pada potensial 0,6 V suhu operasi 90oC adalah: 20% PtCeO2/C (in-house CeO2): 20%, 20% PtCeO2/C (commercial CeO2): 19 %, 20% PtRhCeO2/C (in-house CeO2): 27%, 20% PtRhCeO2/C (Commercial CeO2): 24%.

<i>Direct oxidation fuel cells (DOFCs) have recently attracted major attention, as an alternative to hydrogen fuel cells, mainly due to easier fuel storage and handling. The organic liquids used for DOFCs are much simpler to handle than gaseous hydrogen and also in many cases do not require any new distribution infrastructure. Ethanol is one of the fuel candidates for direct oxidation fuel cell (DOFC). The advantages of ethanol are due to non toxicity, renewability and high energy density. Unfortunately, utilization of ethanol as fuel in direct ethanol fuel cell (DEFC) is still covered by main problem which is slow kinetic reaction due to difficult to break C-C bond in ethanol. In order to solve this main problem in ethanol electro-oxidation reaction (EOR) the research work is aimed to develop and investigate an anode catalyst base on carbon supported platinum catalyst for ethanol electro-oxidation in direct ethanol fuel cell (DEFC) which capable to promote in breaking C-C bond toward total oxidation reaction of ethanol. First specific objective of the research is to study the effect of Rhodium on carbon supported Pt catalysts to the activity and selectivity of ethanol electro-oxidation reaction. The second specific objective is to study the effect of CeO2 on carbon supported Pt catalysts to the activity and selectivity of ethanol electro-oxidation reaction. Moreover, the third specific objective of the research work is to study the effect of Rh and CeO2 addition on carbon supported Pt catalysts to the activity and selectivity of ethanol electro-oxidation reaction. The research methodology was comprised of activities: catalyst syntheses, physical characterization, electrochemical characterization, membrane electrode assembly (MEA), in-situ differential mass spectrometry and fuel cell test in single cell setup. CeO2 nano-size particle material was prepared by two step conventional precipitation (in-house CeO2) and for comparison purpose; we also used commercial CeO2 purchased from Johnson Mattews. Preparation of catalysts (Pt-CeO2/C, Pt-Rh/C and Pt-Rh-CeO2/C) was carried out by

colloidal method using ethylene glycol reductant agent. All of catalysts synthesized with 20 weight percent of Pt loading. New developed catalysts then characterized by SEM-EDX to analyze the morphology of catalysts, X-ray diffraction (XRD) to analyze the crystallography, and transmission electron microscopy (TEM) to investigate the particle size and particle dispersion. Physical characterizations result indicated that in-house CeO2 was a crystallite as CeO2 commercial was with the particle size diameter of about 9 nm, meanwhile the particle size diameter of commercial CeO2 about 19 nm. Particle size diameter of Pt-CeO2/C and Pt-Rh-CeO2/C catalysts was about 2-3.5 nm and well dispersed with light agglomeration. Energy dispersive of X-Ray (EDX) analysis shows that all of element in the catalyst was detected. Electrochemical characterization was carried out by normal cyclic voltammetry, chronoamperommetry, and cyclic voltammetry in present of ethanol either in acid or alkaline medium. Electrochemical characterization is to investigate the activity of the catalyst correlated to the Faradaic current which obtained in half cell/model electrode. In-situ differential electrochemical mass spectrometry (DEMS) was conducted to further investigate the activity and selectivity of ethanol electrooxidation over PtCeO2/C and PtRhCeO2/C in real fuel cell setup. New developed catalysts of PtCeO2/C and PtRhCeO2/C which was synthesized by colloidal method improved the activity and selectivity to CO2 product in ethanol electro-oxidation toward total oxidation reaction in direct ethanol fuel cell. Whereas, effect addition of rhodium in the catalyst was to improve capability in C-C bond breaking, while effect addition of CeO2 in the catalyst was to donor oxygen onto Pt surface to break C-C bond and to promote COads intermediate to the CO2 product on the surface of platinum. Addition of rhodium to the carbon supported Pt catalyst improved in C-C bond breaking in ethanol electro-oxidation. However, the result of C-C bond breaking was not converted to CO2 product totally, due to strongly adsorption of CO intermediate product on surface of PtRh. Therefore, it was only slightly increase of the activity and selectivity of ethanol electro-oxidation reaction (EOR) over PtRh/C compared to commercial Pt/C reference catalyst. Addition of CeO2 to the carbon supported catalyst improved the activity of catalysts in C-C bond breaking and improved the selectivity by promoted the oxidation of CO intermediate product to CO2 on Pt surface. The ceria effect was associated to the capabilities of ceria to provide oxygen on Pt surface that finally could improve activity and selectivity of the catalyst in ethanol oxidation reaction. Addition of Rh and CeO2 to the carbon supported catalyst improved the activity of catalysts in C-C bond breaking and improved the selectivity for CO2 formation. The improvements of activity and selectivity of the catalyst is due to a synergistic effect.In the real fuel cell, improvement of an activity in electrochemical cell measurement was also obtained by in-situ differential electrochemical mass spectrometry. Increase in activity over ceria modified catalyst also led to increase in selectivity for CO2 formation. Increasing in activity was indicated by increment of Faradaic current and the increasing selectivity of the catalysts to the CO2 formation was indicated by increment of the CO2 current efficiency. Both increasing of the activity and selectivity were occurred at low potential less than 0.6 V vs. RHE Increasing activity of ethanol oxidation over ceria modified Pt-based catalysts in comparison to reference catalyst (20% Pt/C) at potential 0.6 V and temperature 90oC are: 20% PtCeO2/C (in-house CeO2): 5.99%, 20% PtCeO2/C (commercial CeO2): 3.89%, 20% PtRhCeO2/C (in-house CeO2): 19.6%, 20% PtRhCeO2/C (Commercial CeO2): 26.3%. The product of the ethanol oxidation reaction over Pt/C, PtCeO2/C, PtRh/C and PtRhCeO2/C which was investigated by in-situ DEMS were CO2, acetaldehyde, methane, ethane. Meanwhile, acetic acid was not detected by DEMS due to low volatility. CO2 current efficiency (CCE) was represented the selectivity to CO2 formation of ethanol oxidation. Increasing CCE over ceria modified Pt-based catalysts in comparison to reference catalyst (20% Pt/C) at potential 0.6 V and temperature 90oC are: 20% PtCeO2/C (in-house CeO2): 20%, 20% PtCeO2/C (commercial CeO2): 19 %, 20% PtRhCeO2/C (in-house CeO2): 27%, 20% PtRhCeO2/C (Commercial CeO2): 24%</i>