Development of High Performance PtCo/C Electrocatalyst for Cathode Proton Exchange Membrane Fuel Cell: Study of Activity and Stability Enhancement by Nitrogen and Carbon Monoxide Treatment

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Abstrak

ABSTRAK
Katalis komersial tidak selalu mempunyai properti yang baik. Katalis ini masih memerlukan perlakuan sehingga dapat memberikan kinerja yang tinggi ketika diaplikasikan pada fuel cell. Metode yang sering digunakan untuk sintesa katalis PtCo/C adalah impregnasi logam pada Platina yang disangga Karbon diikuti proses paduan/alloying pada suhu tinggi. Perlakuan pada suhu tinggi akan menyebabkan aglomerasi sehingga katalis menjadi lebih besar ukurannya, akibatnya terjadi penurunan aktifitas.

Struktur core shell terdiri atas kulit/shell dari suatu atom yang mengelilingi inti/core dari jenis atom yang lain. Struktur ini dapat dicapai melalui proses aneling suhu tinggi, chemical leaching ataupun teknik deposisi elektrokimia. Namun demikian, semua metode tersebut mempunyai kelemahan antara lain berkurangnya luas aktif area, pembentukan shell logam nobel yang tidak lengkap dan memerlukan kontrol potensial selama preparasinya.

Distribusi atom dan alloying extent dari bimetal nanopartikel dapat mempengaruhi aktifitas katalis. Akhir-akhir ini aplikasi x-ray absorption spectroscopy (XAS) banyak digunakan pada bimetal nanopartikel. Namun demikian studi tentang distribusi atom ataupun alloying extent masih terbatas. Pemahaman teori tentang distribusi atom dan alloying extent masih sangat diperlukan.

Tujuan dari studi ini adalah untuk mempelajari peningkatan aktifitas dan stabilitas katalis komersial PtCo/C dengan perlakuan Nitrogen dan Karbon Monoksida untuk mempelajari efek ukuran partikel dan struktur katalis terhadap aktifitas dan stabilitasnya.

Metodologi yang digunakan meliputi perlakuan katalis komersial PtCo/C, karakterisasi fisik, karakterisasi kimia serta pengujian kinerja sel tunggal. Katalis dilakukan perlakuan dengan Nitrogen pada berbagai macam suhu untuk mengetahui efek ukuran partikel terhadap aktifitas dan stabilitasnya, serta perlakuan dengan Karbon Monoksida pada berbagai macam waktu untuk mengetahui efek struktur katalis terhadap aktifitas dan stabilitasnya. Karakterisasi fisik yang dilakukan adalah x-ray diffraction (XRD), transmission electron microscopy (TEM) dan XAS. Sedangkan karakterisiasi kimia yang dilakukan adalah cyclic voltammetry (CV) dan linear sweep voltammetry (LSV).

Analisa XRD yang dilakukan pada katalis PtCo/C dengan perlakuan Nitrogen menunjukkan bahwa ukuran partikel menjadi lebih besar dengan bertambahnya suhu perlakuan. Analisa TEM menggambarkan distribusi partikel yang merata dan sesuai dengan hasil XRD. Sedangkan, analisa elektrokimia menunjukkan kurva voltammogram yang bentuknya seperti kurva voltammogram Pt.

Untuk katalis PtCo/C dengan perlakuan Karbon Monoksida, analisa XRD menunjukkan bahwa adanya puncak Kobal untuk katalis dengan perlakuan selama 5, 7, 10 dan 15 jam. Hal ini mengindikasikan adanya segregasi ke permukaan katalis. Analisa XAS memberikan hasil struktur Pt rich in core Co rich in shell untuk katalis dengan perlakuan selama 1, 3 dan 5 jam. Sebaliknya perlakuan selama 7, 10 dan 15 jam menghasilkan struktur Pt rich in shell Co rich in core. Dari analisa elektrokimia yang dilakukan, dihasilkan tidak adanya perubahan CV untuk katalis dengan perlakuan selama 1-5 jam, mengindikasikan adanya peningkatan aktifitas. Sebaliknya perlakuan selama 7-15 jam menunjukkan katalis bersifat kurang aktif. Pengujian stabilitas menunjukkan katalis dengan perlakuan 1-5 jam bersifat tidak stabil. Hal ini dikarenakan Pt yang terletak di core tidak mampu untuk melindungi Co yang berada di shell dari disolusi. Sebaliknya katalis dengan perlakuan selama 7-15 jam bersifat stabil, karena Pt yang terletak di shell mampu melindungi Co yang berada di core dari proses disolusi.

Pengujian kinerja sel tunggal menunjukkan bahwa katalis dengan perlakuan Karbon Monoksida selama 3 jam merupakan katalis yang mempunyai kinerja terbaik. Hal ini sesuai dengan aktifitas masa dan luas permukaan spesifik dari katalis dengan perlakuan Karbon Monoksida selama 3 jam, di mana katalis ini mempunyai aktifitas paling baik terhadap reaksi reduksi oksigen. Terlihat bahwa terjadi peningkatan power densitas sebesar 20,49 %, di mana katalis PtCo/C komersial mempunyai power density 88,33 mW/cm2 dan katalis PtCo/C dengan perlakuan Karbon Monoksida selama 3 jam mempunyai power density 108,82 mW/cm2.
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ABSTRACT
The synthesis procedure on a commercial catalyst still needs to be improved in order to get a better catalyst performance for application on fuel cell. There is no guarantee that the commercial catalyst has a good property. The commonly used method to prepare PtCo/C electrocatalyst is through impregnation of the second metal on platinum supported carbon (Pt/C) followed by alloying at high temperature in an inert gas. This high temperature heat treatment facilitates the growing of the alloy nanoparticles (NPs) due to sintering, which is undesirable because it may result in reduction of the Pt mass activity for the oxygen reduction reaction (ORR).

Core shell NPs consist of a shell of one type of atom surrounding a core of another type of atom. This structure can be achieved by high temperature annealing, chemical leaching of the non noble material or electrochemical deposition technique.

Nevertheless, all of these methods exhibit significant disadvantages such as losses in active surface area and material, formation of an incomplete noble metal shell, and necessity for potential control during preparation.

It is important to understand the atomic distribution and alloying extent of participating elements in individual bimetallic NPs, as these factors also influence the intrinsic catalytic activity. In recent years, x-ray absorption spectroscopy (XAS) studies have been well explored on bimetallic NPs. However, XAS studies focusing on estimation of atomic distributions or alloying extent in the NPs are limited. Therefore, we propose a methodology to estimate the structural characteristics such as alloying extent or atomic distribution in bimetallic NPs, by deriving the structural parameters from XAS analysis and to demonstrate the results on commercially available carbon supported PtCo NPs.

The overall objective of this study is to enhance the activity and stability of commercial PtCo/C electrocatalyst through treatment with nitrogen (N2) and carbon monoxide (CO). In this work, a commercial PtCo/C catalyst was treated using two different strategies to study the effect of particle size and structure on its activity and stability The research methodology consists of PtCo/C catalyst treatment, physical characterization, electrochemical characterization and single cell proton exchange membrane (PEM) fuel cell performance test. The catalysts were treated with nitrogen at various temperatures in order to study the effect of the particle size on its activity and stability, and also treated with carbon monoxide at various times in order to study the effect of the structure on its activity and stability. Physical characterizations were done through x-ray diffraction (XRD), transmission electron microscopy (TEM) and XAS. The electrochemical characterizations were done using cyclic voltammetry (CV) and linier sweep voltammetry (LSV).

For the PtCo/C that is subjected to N2 treatment, XRD result shows the particle size is increased with increasing temperature of treatment. TEM result shows that all the PtCo NPs are well dispersed on the surface of carbon and it is in accordance with the XRD result. The electrochemical characterization shows that the base voltamogram becomes more Pt-like, which is indicative of leaching Co from the surface. While for PtCo/C that is subjected to CO treatment, the XRD result shows that treatmnet for 5, 7, 10 and 15 hours leads to surface segregation, at which the peak of Co-related species is clearly observed. The alloying extent and coordination number of the catalysts were investigated with XAS, show that treatments for 1, 3 and 5 hours resulted in Pt rich in core Co rich in shell. On the contrary, treatments for 7, 10 and 15 hours resulted in Pt rich in shell Co rich in core.

It is clearly demonstrated that the PtCo/C subjected to CO treatment for 1-5 hours shows the enhanced ORR activity, but the catalyst is unstable due to the dissolution of Co, while samples treated for 7-15 hours display poor activities. However, the catalyst is stable, which is likely due to the fact that Pt in the surface protects Co from dissolution.

The single cell PEM fuel cell performance test shows that PtCo/C subjected to CO treatment for 3 hours shows the best performance. This result is in accordance with the specific surface area and mass activity of PtCo/C that is subjected to CO treatment for 3 hours, which has a better activity toward ORR. Catalyst treatment would increase the fuel cell performance by 20.49 % (Power density of commercial PtCo/C electrocatalyst: 88.33 mW/cm2, PtCo/C electrocatalyst subjected to CO treatment for 3 hours: 108.82 mW/cm2)</i>