Current Development In Ethanol Fuel Cell

Introduction

Determining a favorable pathway is one of the important steps in designing a catalyst for a fuel cell. Direct ethanol fuel cell is an attractive power source due to its high energy density for fuel cell systems. Each ethanol molecule can release 12 electrons via multiple oxidation and dehydrogenation step which involve cleavage of C-C bond. Various catalyst combinations were studied to improve EOR efficiency through higher selectivity, high peak current and lower onset potential. This study is mainly focused on recently derived ternary catalyst consisting of Au (works as a core) and PtIr (works as a shell) supported on carbon.

Synthesis

On carbon-supported Au (Au/C) nanoparticle researcher synthesized PtIr at a temperature around near to boiling point. Due to this a well mixed layer of atoms of Pt and Ir takes place over the Au nanoparticle. They are mixed in a molar ratio of 10:1:1(Au: Pt: Ir).

From Fig (1a) it can be seen that our core-shell nanoparticle shows XRD peaks close to FCC Au indicate that Ir and Pt atoms are in alignment with Au lattice. The tensile strength obtained from peaks are 3.8 % w.r.t. Pt and 6.1% w.r.t. Ir which are close to 4.1% and 6.3% (of lattice mismatch)

Fig (1b) the TEM analysis given in fig 1b proves the narrow distribution of particle size (±1.8 nm) with a structure of Au = {111}. The atomic ratio of surface to the core is 5.8 ± 1.8 nm and (Pt + Ir)/Au ratio is 0.17 which confirms that PtIr shell is in the monatomic island form.

Fig (1 c-f) shows the particle distribution of Au –PtIr. The results revels that the particle from Pt (in blue color) and Ir (in green color) spread evenly and they are much less intense in the center as compared to that of Au (in pink color) . This proves that the formation of thin layer by Ir and Pt on Au core.

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Figure 2a shows an EOR current peak of 58 (A mg?1 PGM) obtained by using the Au - PtIr/C catalyst. It is performed in 1 Methanol and 1 M KOH solution. The peak value is 8 and 38 times the peak value of Au-Pt/C and Au-Ir/C, respectively.

Figure 2b The Au-PtIr/C catalyst shows0.52 (A mg ?1) at 0.6 V which is 4.3 times that of PtIr/C, for this measurements gas di?usion electrodes were used. Further, this study is focused on the performance of EOR below 700mV and reversible and high current up to700mV in Au-PtIr is a good indication of practical anode catalyst at normal temperature.

Figure 2c it can be seen that from fig 2c addition of CNT will lower the potential of EOR but it will increase current below 0.55V. Most likely it is due to the enhancement of OH transport which is

responsible for dehydrogenation.

Figure 2d chronoamperometry curve shown in fig 2d which is measured at 0.45eV for Au/PtIr catalyst in the absence of CNT. A quasi-steady state is reached after 15 min by an intermediate of EOR

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Feature Indication

- a Spectra are seen during the positive potential sweep. C1-12e pathway is active on the ternary catalyst
- b Bipolar band for Au-PtIr/C -
- c Linear adsorption of CO 1) Indirect 12e oxidation can be completed at high potential.

2)Oxidation of CO is the rate-limiting step

- d Larger bipolar band if formed at1046 cm-1 for PtIr/C _
- f bipolar band if formed for Au-PtC -

SELECTIVITY OF PATHWAY

CO2 reacts with OH- to form carbonate in the alkaline medium as shown by following figure C-12 pathway is found by C-C bond splitting by ethanol dissociative adsorption which gives hydrogen-rich C1 fragment that can be fully oxidized without the poisoning of intermediate. In C2 -4e pathway adsorption of nondissociative ethanol takes place followed by dehydrogenation with or without C-C bond splitting. The pathway in which C-C bond splits after the dehydrogenation and it can absorb CO as a major intermediate.

Structural And Compositional Effects On Eor Specific Activity

Fig 5. a shows the voltammetry curve over the normalized surface area. Here they used calculated geometric area because adsorption of hydrogen is relatively stronger on PtIr/C than core shell catalytic area. The calculations are performed by considering spherical metal particle and the diameter were calculated by XRD. In fig 5b EOR specific peak currents are shown by the height of bar v/s corresponding peak potential. They notice that particle with size in nanometer can prove to be highly active for many heterogeneous reactions.eg. Au particle with size 4.5nm has approx 10 atoms at each of the 24 edges which are approx 20% surface atoms. For acid, the CO2 band at 2343cm-1 is observed for EOR with Pt monolayer on Au nanoparticle. Therefore ethanol dissociation is preferred at the monatomic step of Pt or PtIr Island. Mostly it is near the edge of Au nanoparticles. At high potential tensile strain is proves to be highly effective to promote EOR current in acid. As compare to Pt the monolayer of Pt on Au shows 4 fold peak current. While Pt monolayer on Pd, Ir, Rh, Ru shows lower peak current.

Thus oxidation of C1 or C2 intermediate proves to be beneficial to enhance the OH and water adsorption in base and acid resp. in this study higher order EOR activity on Au- PtIr is observed in core-shell catalyst than the Au- PtIr alloy catalyst. This promotes the importance of direct C1 pathway and the tensile strength to improve the oxidation of reaction kinetics. On the other hand

Iridium proves to be the promoter for the dehydrogenation process which ultimately lowers the onset potential. According to density function theory iridium is one of the best metals for the dehydrogenation of ammonia. According to DFT calculation, Ir offers a high barrier in the formation of CH3COOH from CH3CO + OH (high barrier for unfavorable reaction, C2?4e pathway.) and it has the lowest barrier for C?C bond cleavage in CHCO to form CH + CO (low barrier in favorable reaction C1?12e pathway).

Conclusion

A ternary core shell catalyst (Au-PtIr/C) shows extraordinary EOR performance using an alkaline solution. It exhibits high peak current at 58A mg-1, the lowest onset potential of 0.3 V and high percentage C1 -12e pathway current of 57%. Au-PtIr core-shell catalyst has a catalytic activity which is six order of magnitude greater than Au-PtIr alloy catalyst proves structural sensitivity of kinetics of EOR and effectively activate C1 -12e pathway. Lattice expansion of Au core and PtIr monolayer island responsible for ethanol adsorption at low potential. Ir plays an important role in dehydrogenation reaction. Thus Au-PtIr is proved to be an ideal catalyst for EOR with excellent efficiency.

References

Direct 12-Electron Oxidation of Ethanol on a Ternary Au(core)PtIr(Shell) Electrocatalyst (Journal of the American chemical society) Zhixiu Liang, Liang Song, Shiqing Deng, Yimei Zhu, Eli Stavitski, Radoslav R. Adzic, Jingyi Chen,? and Jia X. Wang.(DOI:10.1021/jacs.9b03474).