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Direct Ethanol Fuel Cell (DEFC) Assembled with Ceramic Membrane-Catalyst

Back-Sub Sung[1], Young-Hoon Yun[2], *

[1]Dept. of Mechanical Engineering, Chosun University, Gwangju, Korea

[2]Dept. of Hydrogen & Fuel Cell Tech., Dongshin University, Jeonnam, Korea

Email address:

yunh2@dsu.ac.kr (Young-Hoon Y.)

*Corresponding author

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Abstract: Direct ethanol fuel cell (DEFC) has been assembled with the ceramic membrane based-Pt/C (40wt%) catalyst electrodes. The porous silicon carbide (SiC) membrane, fabricated through sintering process, was applied for the fabrication of DEFC. The dilute ethanol-water fuel solution was used for the DEFC operation with a micropump and air blower. The direct ethanol oxidation based-ceramic membrane fuel cell showed relatively stable potential-current behavior even though at room temperature by a continuous air-blowing and a circulation of the dilute-ethanol fuel solution. The other chemicals such as acetaldehyde or acetic acid, being formed during DEFC operation, was not detected from the NMR (nuclear magnetic resonance) spectrum analyzed with the dilute ethanol fuel solution collected upto 90min.

1. Introduction

Direct Ethanol Fuel Cell (DEFC), referred as a PEM-based direct alcohol fuel cell, is promising candidates as power sources especially at small-scale applications such as mobile phones as well as commnercial drones [1]. Especially, a direct alcohol fuel cell/battery hybrid system will become standard equipment for new-type drones [2]. As new electricity-supply equipments for hydogen-powered drones, direct alcohol (methanol or ethanol) fuel cells (DMFC or DEFC) and polymer electrolyte membrane fuel cell (PEMFC) have been developed [3]. The ethanol–water mixture aqueous solutions are fed to the anode compartment of the DEFC, where with the aid of the electrocatalysts, ethanol is oxidized to produce carbon dioxide releasing simultaneously protons and electrons [4-5]. Protons are then transported to the cathode through the electrolyte and electrons flow through an external circuit, and then arrive at the cathode [6-7].

There are two basic types of DEFC concepts: PEM-based and AEM-based (AEM = anion-exchange membrane). The main challenge for the PEM-based concept is the slow kinetics of the ethanol oxidation at the anode [8-9]. An AEM-based concept shows faster kinetics for both the ethanol oxidation and the oxygen reduction reaction (ORR) than the PEM-based concept, and higher efficiencies have been shown [10-14].

By comparing the performance of fuel cells operating on some low molecular weight alcohols, it was resulted that ethanol may replace methanol in a direct alcohol fuel cell. This study is to identify the potential in the direct ethanol fuel cells (DEFC) application. To improve the performance of a direct ethanol fuel cell (DEFC), it is of great importance to develop anode catalysts for ethanol electro-oxidation more active than platinum alone [9]. The major problem in the fabrication and commercialization of DEFCs is connected to the swelling and distortion of the polymer membrane [10-11]. The present polymer electrolyte membrane has some problems such as a swelling and a distortion with a geometrical resistance in the crossover of ethanol. The present polymer membrane for DEFC or PEMFC should be replaced by SiC ceramic membrane. The establishment of the DEFC membrane technology would be able to applied to the field of small electronic devices and their power source. DEFC system have some merits in the view of fuel supply & storage as well as replacement

compared to other fuel cells. DEFC system shows low operation temperature and high current density as well as rapid starting and response to load variation, the utilization and dissemination of DEFC system in small or portable electronic devices is expected through these research programs [12-18].

The present research is to develop a direct ethanol fuel cell (DEFC) using silicon carbide mebrane-based catalyst electrode assembly. The ceramic membrane-catalyst assembly to substitute the previous polymer membrane was made for fabricating the DEFC. The DEFC system comprised of the membrane electrode assembly (MEA) using silicon carbide (SiC) membrane was characterized, its power output was measured. During the demonstration test, the ethanol-water fuel solution circulated through the DEFC system was analyzed by NMR.

2. Experimental Procedure

SiC membrane was fabricated by heating SiC powders (mean sizes of 10μm) with silicon resin. A porous silicon carbide (SiC) membrane having approximately 30% has been applied for making up a direct ethanol proton exchange membrane (DE-PEM) fuel cell. A horizontal type cell having Pt/C (40wt%) catalyst layer on both side of the ceramic membrane was used for the demonstration test. Pt/C catalyst ($18mg/cm^2$), nafion solution (100mg, 5wt%) and IPA (isopropyl alcohol, 300mg) was mixed and then spreaded on the ceramic membrane. Carbon cloth containing Pt/C catalyst was attached on both side of the ceramic membrane and catalyst electrode Pt/C. The MEA and graphite end plates was compressed. The power output was measured by supplying dilute-ethanol fuel solution with continuous air-blowing condition at room temperature. During operation of DEFC, the samples of dilute-ethanol fuel solution were taken for NMR analysis to identify the intermidiate phase, being created from the dilute-ethanol fuel solution.

3. Result and Discussion

In this research, the SiC ceramic membrane based-direct ethanol fuel cell was fabricated with Pt/C catalyst electrode and graphite end plates.

Figure 1 shows photograph and FE-SEM surface morphology of SiC ceramic membrane. Porous microstructure having a pore size range of 20-40 μm was observed in the SiC ceramic membrane fabricated as the thin plate type of 40×40×5mm size. This research is to produce the membrane electrode assembly (MEA) using silicon carbide (SiC) membrane, catalyst, anode and cathode. A horizontal type cell having Pt/C (40wt%) catalyst layer on both side of the ceramic membrane having approximately 30% was used for the demonstration test.
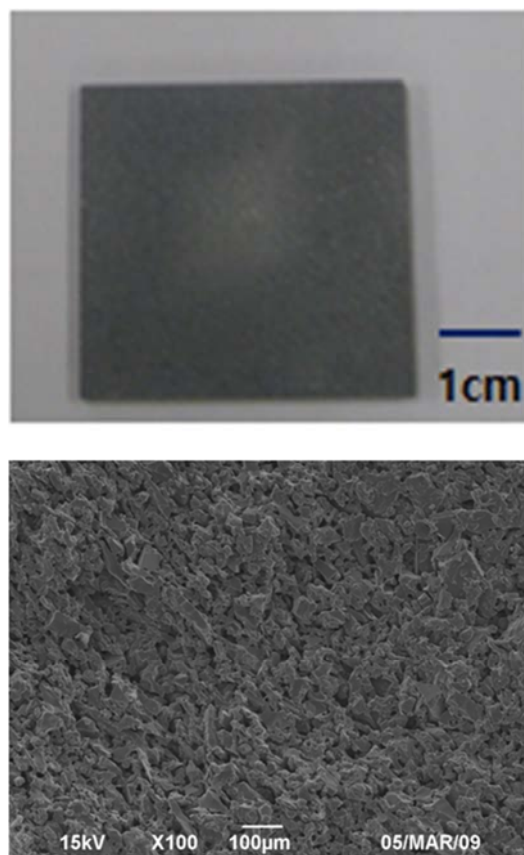

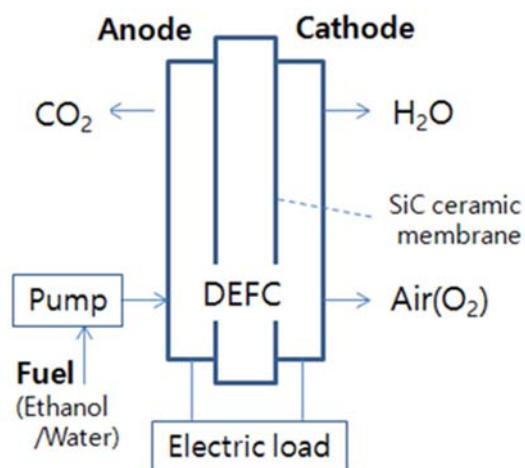Figure 1. Image and FE-SEM morphology of porous SiC ceramic membrane for DEFC.

Figure 2. Schematic diagram of DEFC fabricated with SiC ceramic membrane.

Figure 2 and Figure 3 show schematic diagram and layout design of collector, MEA and end plate of DEFC. The Pt/C catalyst electrode layers and SiC ceramic membrane of 5mm thnickness was assembled with metal frames. The DEFC system was designed in the configuration of having micropump for injecting the dilute ethanol fuel solution into it.
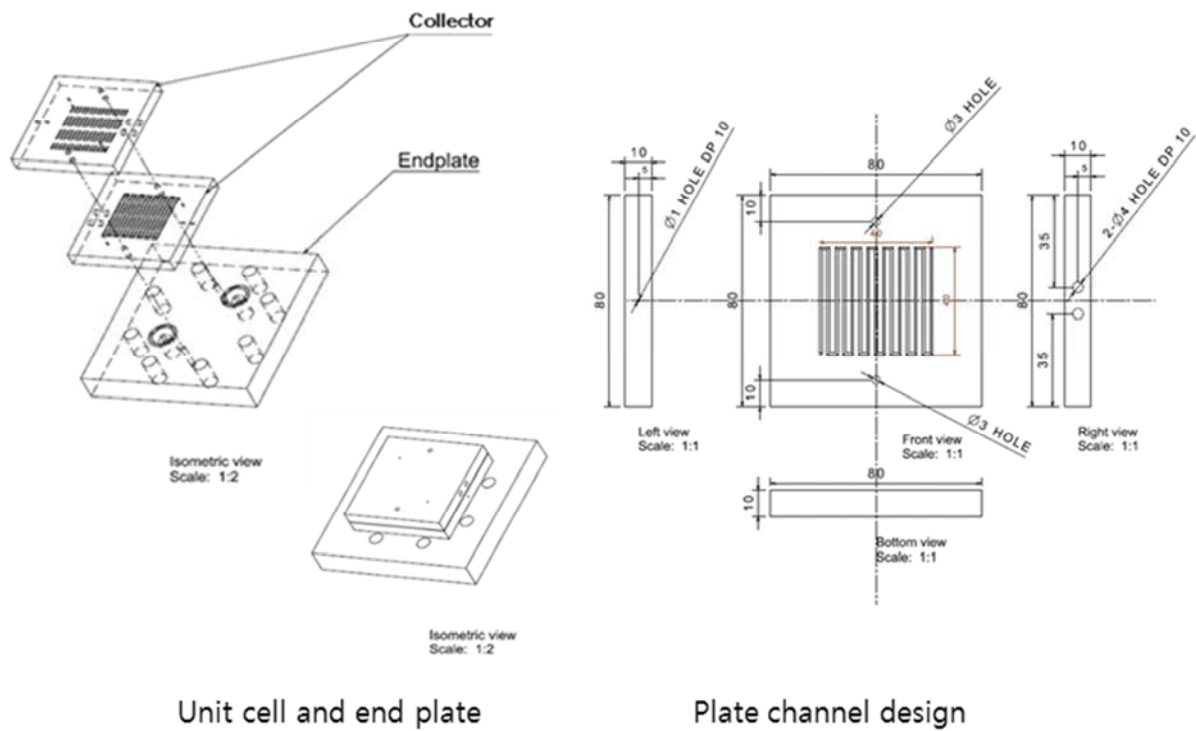
Figure 3. *Design of DEFC fabricated with SiC ceramic membrane and fuel cell parts.*
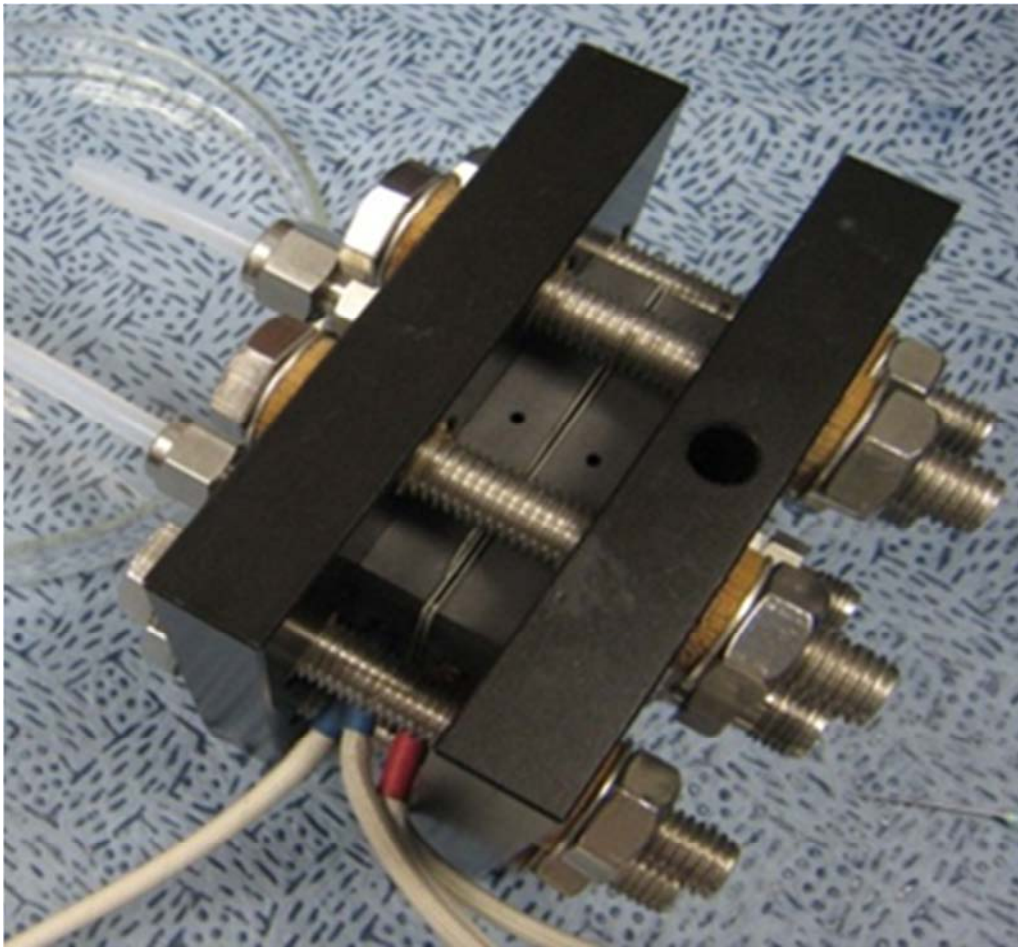
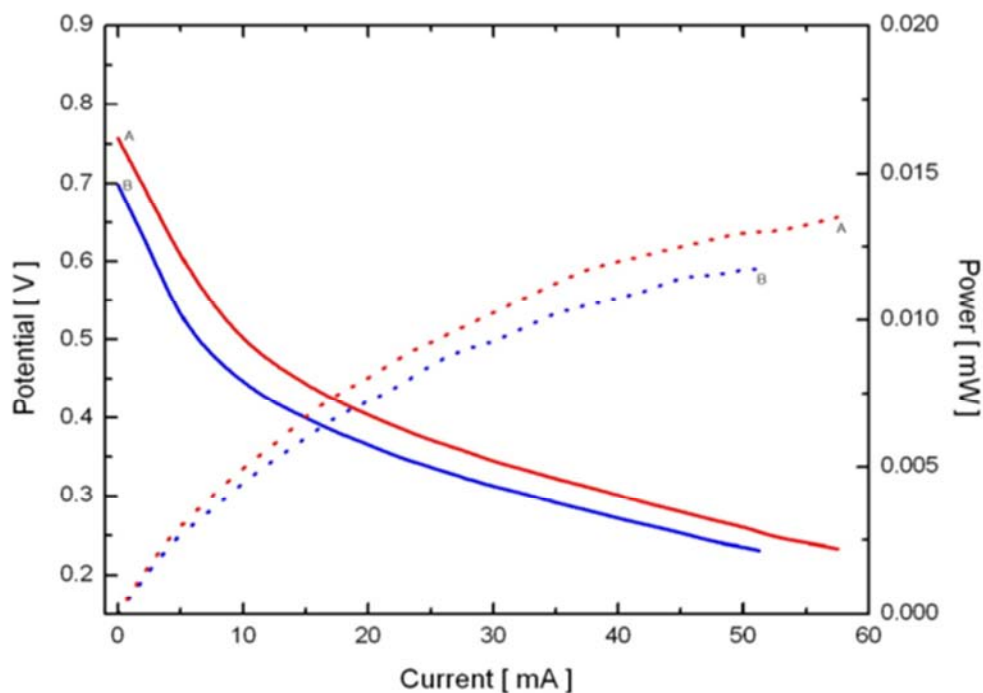**Figure 4.** *DEFC fabricated with SiC ceramic membrane.*

Figure 5. *Cell potential vs. current behavior of direct ethanol fuel cell for ethanol solution.*

Figure 4 shows DEFC system fabricated with SiC ceramic membrane and catalyst. Figure 5 shows performance results, cell potential and current behavior of DEFC operation for dilute ethanol fuel solutions with different ethanol concentration of 2wt% and 5wt%. In the initial experiment, DEFC was fabricated with relatively dense SiC ceramic membrane and the voltage increased into 245.9 mV without electrical current level. It seemed in case of dense SiC membrane that the oxidation and reduction of ethanol was not sufficient for obtaining electrical current. In the voltage-current and power-current of direct ethanol fuel cell, the voltage drop of the direct ethanol fuel cell was observed with increasing current. The sufficient feeding of aqueous ethanol solution into direct ethanol fuel cell stack exhibited very high voltage and high current level of 1.289 V, 1.11A through simple multi-meter.

The excess fuel feeding by micropump induced problem of leakage of the dilute ethanol solution by alcohol cross-over and accumulation of liquid fuel in membrane. The output with the concentration of the dilute ethanol solution and operation time was nearly constant. During DEFC, the maximum current increased to 1.11A and maximum power density showed 88.6 mW·cm^{-2} at room temperature. Upto now, the power density, reported concerning DEFC, 30mW·cm^{-2} (25°C) in case of alkaline type and 50mW·cm^{-2} (60°C)[18], 185 mW·cm^{-2} (80°C)[19], 38.6mW·cm^{-2} (80°C)[20] for multi walled carbon nanotubes. The performance of fuel cells is represented in its cell potential versus current. This behavior is largely determined by the kinetics of the electrode reactions and the internal resistance of the cell. The potential loss due to the slow kinetics associated with oxygen reduction electrode was revealed as curves in the line of potential-current behavior. Also, the smooth potential drop

due to internal resistances was shown in the diagram. The cell potential measured was rather low as compared to the values measured by simple multimeter, due to the problems of electrical resistance and electrode-contact in electrode for measurment. The internal resistacne of DEFC showed somewhat fluctuation in power output of cell.

Generally, the liquid solution at the anode may create the problem of the catalyst layer readily peeling off from the solid polymer electrolyte (SPE) membrane, i.e. ''electrode delamination'', due to the different swelling degree between polymer membrane and the electrode. The ceramic membrane would prevent the problem related to the electrode delamination in DEFC. This study is concerned with fabricating new membrane electrode assembly (MEA) showing active Pt/C catalyst layer, porous anode electrode and porous ceramic membrane. In this research, the electrtical voltage and current were relatively stable during DEFC operation for 10hrs. This behavior implies the long-time durability for dilute ethanol soultion of the SiC ceramic membrane of the DEFC. However, there is no report about the modification or adopting new electrolyte to avoid or at least decrease ethanol crossover to some degree.

The ethanol oxidation based-fuel cell stack showed high voltage and measurable current level even though at room temperature. Even if, the porous ceramic membrane was utilized for the direct ethanol-proton exchange membrane fuel cell, low permeability of the ceramic membrane for ethanol as compared to the conventional polymer electrolyte would occur. It was inferred in case of the porous ceramic membrane, the current material exhibit somewhat alcohol cross-over to the cathodic electrode greatly decreasing cell efficiency.

Generally, it was reported the ethanol don't completely

decomposed into CO_2 and H_2O but will convert acetaldehyde (CH_3CHO), acetic acid (CH_3COOH) with small amount as intermediate phases in electrochemical oxidation below 100°C [17, 21]. However, in DEFCs below 100°C the electro-oxidation of ethanol does not proceed all the way to carbon dioxide (CO_2), but rather to acetaldehyde (CH_3CHO),

acetic acid (CH_3COOH), and CO_2 depending on the nature and structure of the catalyst used, the applied potential, and the temperature field established. Acetaldehyde was reported to be the main product of ethanol oxidation in early investigations.
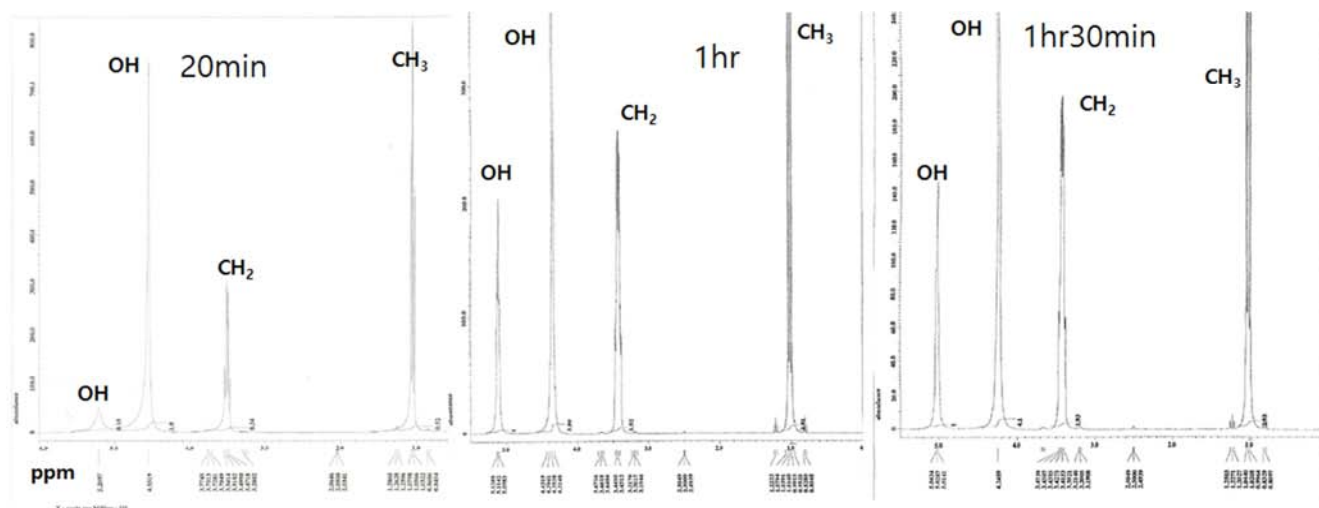

Figure 6. 1H NMR spectra of the dilute ethanol solutions taken after DEFC operation.

Figure 6 shows the NMR spectrum analyzed with the dilute ethanol fuel solution collected after DEFC operation for 15minutes. Other chemicals besides ethanol did not detected by NMR analysis. The pattern differences between the initial fuel solution and the colleted ethanol fuel solution were identified in NMR data. Even though, the acetaldehyde and acetic acid have been created from the ethanol during operation, these chemicals would be a very small quantities and might be decomposed in a short period of time. From the fundamental research to the development of electrode materials and fuel cell assembly until the introduction of fuel cell into commercialization, the investigation on all possible factors affecting the DEFC's performance and stability are just at initial stage, and there is still much works to improve for direct ethanol fuel cell development.

4. Conclusion

In this study, ceramic electrolyte membrane (CEM)-based DEFC was developed with Pt/C catalyst electrode layer. The DEFC having 18 mg/cm^2 Pt (40 vol.%)/C catalyst layer on both side of the ceramic membrane was used for the demonstration test. The ethanol oxidation based-fuel cell stack showed measurable voltage and current level even though at room temperature. The DEFC fabricated with dense SiC membrane didn't showed the electrical current showing voltage level of 245.9 mV. Using porous SiC membrane, the DEFC showed mearsurable voltage and current level of 1.289 V, 1.11A and maximum power density of 88.6 mW•cm^{-2} at room temperature. The NMR analysis for circulated dilute ethanol solution obtained from DEFC demonstration test did not revealed the presence of other chemicals being decomposed from

ethanol.

Acknowledgment

References

[1] Badwal S. P. S., Giddey S., Kulkarni A., Goel J., Basu S., Direct ethanol fuel cells for transport and stationary applications – A comprehensive review, Applied Energy, 145 (2015) 80-103.

[2] Nancy O., (2015, December 16) Hydrogen fuel cells may turn corner in commercial drone use Retrieved from https://techxplore.com/news/2015-12-hydrogen-fuel-cells-corner-commercial.html.

[3] Kamarudin M. Z. F., Kamarudina S. K., Masdar M. S., Daud W. R. W., Review: Direct ethanol fuel cells, Int. J. of Hydrogen Energy, 38 (22) (2013) 9438–9453.

[4] Larminie J., Dicks A., Fuel Cell Systems Explained, 2nd ed., Wiely, 20-50, 2003.

[5] Song S., Tsiakaras P., Recent progress in direct ethanol proton exchange membrane fuel cells (DE-PEMFCs). Appl. Catal. B: Environ. 63, 187–193, 2006.

[6] Wang Z., Yin G., Zhang J., Sun Y., Shi P., Investigation of ethanol electrooxidation on a Pt–Ru–Ni/C catalyst for a direct ethanol fuel cell, J. Power Sources 160, 37–43, 2006.

[7]   Zhou W., Zhou Z., Song S., Li W., Sun G., Tsiakaras P., Xin Q., Pt based anode catalysts for direct ethanol fuel cells, Appl. Catal. B: Environ. 46, 273–285, 2003.

[8]   Zhao X., Jiang L., Sun G., Yang S., Yi B., Qin X., Electrocatalytic property of Pt-Sn catalyst for electro-oxidation of ethanol, Chin. J. Catal. 25, 983–988, 2004.

[9]   Antolini E., Catalysts for direct ethanol fuel cells, Catalysts for direct ethanol fuel cells, J. Power Sources, 170 (1), 1-12, 2007.

[10]   Andreadis G., Stergiopoulos V., Song S., Tsiakaras P., Direct ethanol fuel cells: The effect of the cell discharge current on the products distribution, Appl. Catal. B, 100, 157-164, 2010.

[11]   Spinace E., Linardi M., Neto A., Co-catalytic effect of nickel in the electro-oxidation of ethanol on binary Pt–Sn electrocatalysts, Electrochem. Commun. 7, 365–369, 2005.

[12]   Colmati F., Antolini E., Gonzalez E., Effect of temperature on the mechanism of ethanol oxidation on carbon supported Pt, PtRu and Pt3Sn electrocatalysts, J. Power Sources 157, 98–103, 2006.

[13]   Colmati F., Antolini E., Gonzalez E., Ethanol oxidation on a carbon-supported Pt75Sn25 electrocatalyst prepared by reduction with formic acid: Effect of thermal treatment, Appl. Catal. B: Environ. 73, 106–115, 2007.

[14]   Berg H., Nyman J., Erlandsson P., Johansson P., Matic A., Direct Ethanol Fuel Cells: Ethanol for our future fuel cells, Energiforsk AB, Stockholm, 2015.

[15]   Lamy C., Lima A., Lerhun V., Delime F., Coutanceau C., Leger J. M., Recent advances in the development of direct alcohol fuel cells (DAFC), J Power Sources, 105, 283-296, 2002.

[16]   An L., Zhao T. S., Performance of an alkaline-acid direct ethanol fuel cell, Int. J. Hydrogen Energy, 36, 9994-9999, 2011.

[17]   Kim I., Han O. H., Chae S. A., Paik Y. K., Kwon S. H., Lee K. S., Sung Y. E., Kim H. S., Catalytic Reactions in Direct Ethanol Fuel Cells, Angewandte Chemie International Edition, 50, 2270-2274, 2011.

[18]   Yang C. C., Chiu S. J., Lee K. T., Chien W. C., Lin C. T., Huang C. A., Study of poly (vinyl alcohol)/titanium oxide composite polymer membranes and their application on alkaline direct alcohol fuel cell, J. Power Sources, 184, 2008, 44-51.

[19]   Brouzgou A.. Podias A.. Tsiakaras P., PEMFCs and AEMFCs directly fed with ethanol: a current status comparative review, J Appl Electrochem, 43, 2013, 119-136.

[20]   Jafri R. I., Ramaprabhu S., Multi walled carbon nanotubes based micro direct ethanol fuel cell using printed circuit board technology, Int. J. Hydrogen Energy, 35, 2010, 1339-1346.

[21]   Tayal J., Rawat B., Basu S., ‘Bi-metallic and trimetallic Pt-Sn/C, Pt-Ir/C, Pt-Ir-Sn/C catalysts for electro-oxidation of ethanol in direct ethanol fuel cell’, Int. J. Hydrogen energy, 36, 2011, 14884-14897.