Incorporation of zeolite as a proton conductor in the catalyst for electro-oxidation of methanol

메탄올 전기 산화를 위한 프르톤 컨덕터 촉매로써의 제올라이트 혼합

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1. Introduction

Direct methanol fuel cell (DMFC) is being widely investigated and considered as a possible power source for small-power distributed generators and portable applications[1]. Despite a significant progress of the principle of DMFC, it still delivered low power density, which has been attributed by low-activity of anode catalysts. In the literature, Pt-Ru catalyst has been used extensively for electro-oxidation of methanol[2]. zeolites have very large surface area, thermal stability and ion-exchange. Remembering the fact of zeolites having large surface area, high thermal stability and ion exchange abilities, it can use as anode catalyst for DMFC. In the existing literature, there is no such reported information, to the best of our knowledge. In this study, zeolites were used with PtRu/C catalyst for the electro-oxidation of methanol as a new type of proton conductors. For the fast screening of zeolites loading on PtRu/C, high-throughput-screening test was carried out[3]. Impedance spectra analysis of DMFC anode was also carried out with the help of impedance spectroscopy (Autolab's of potentiostat)[4]. The operation of DMFC with the PtRu/C-zeolite(ZSM-5) catalyst were performed to understand the effect of zeolite on the electrochemical properties of PtRu/C.

2. Experimental

To prepare the electrode arrays, commercial PtRu/C (Pt : Ru : C = 40 : 20 : 40, wt%) received from E-Tek was mixed with zeolites. It was then deposited onto a Teflon-coated Toray carbon sheet as shown in Fig. 1. The array was dried at room temperature for 12h. The electrolyte

solution was composed of 6M of methanol, of which the pH was adjusted to 7[3]. Finally, quinine solution (100μM) was added to the electrolyte solution as a proton indicator. The array was used as a working electrode and the carbon paper was as counter electrode. The potential sweep between -0.3V and 1.0V at the rate of 20mV/s was carried out using potentiostat/galvanostat. The most active working electrode was selected by the brightest spot of the array obtained by florescence emission excited by UV of 254nm. A single direct methanol fuel cell was operated at a various temperature, with an active area of 0.25cm^2. The anode catalysts were PtRu/C (Pt : Ru : C = 40 : 20 : 40, E-Tek) and zeolite(ZSM-5) with PtRu : zeolite(ZSM-5) = 7 : 3. For the cathode, Pt/C (Pt : C = 60 : 40, E-Tek) was used. Membrane-electrode assembly (MEA) was fabricated by a hot pressing method for 6min at 125℃, 2.5 Metric ton (1500psi). The feed flow rate of the anode was 1.0ml/min of 2M methanol solution, and cathode gas (oxygen) was maintained at 300ml/min. To analyze the DMFC anode impedances, the anode was supplied with a 2M aqueous solution of methanol at the 1.0ml/min flow rate. The cathode was operated on hydrogen, which serves as a reference and counter electrode. For impedance measurement, the current was modulated by a small sinusoidal signal so that the potential amplitude did not exceed 15mV. Impedance spectra were usually obtained at frequencies between 40 kHz and 3mHz. The electrochemical cell was connected to an AUTOLAB FRA2 impedance analyzer for electrochemical impedance spectroscopy.

3. Results and discussion

The zeolites(A, X, Y, ZSM-5)were well-mixed with PtRu/C in various ratios. The mixture was deposited and reduced on carbon paper to prepare electrode array. Figure 2 shows the fluorescence images of PtRu/C zeolites array for electro-oxidation of methanol at various potentials. The fluorescence of PtRu/C-zeolite spot was distinguishable from 0.3V. The first spot denotes for PtRu only. The other spots are for electro-oxidation of methanol. Among the all types of zeolites, ZSM-5 spots the most active composition(7 : 3). At the potential of 0.4V, the spots of PtRu : zeolites = 9 : 1, 8 : 2, 7 : 3 were brighter than the other spots. The addition of zeolites lowered the intial

oxidation potential of methanol. This indicates that zeolites helped the methanol electro-oxidation of platinum. However, the zeolites-only-catalyst (the last spot) never emitted any fluorescence which indicates that the acidic proton was not formed on zeolites-only-system. We prepared DMFC catalysts of PtRu : ZSM-5 = 7 : 3. It is to be noted that when the catalyst in anode is PtRu/C-zeolite(ZSM-5), the catalyst in cathode is Pt/C. Figure 3 shows the single direct methanol fuel cell performance (Area of MEA = 0,25cm^2) of various temperatures PtRu/C-zeolite(ZSM-5) as anode (Figure 3b) showed higher performance than commercial PtRu/C as anode (Figure 3a) above 10 0℃operation of DMFC. The enhanced performance should be attributed by addition of zeolite (ZSM-5) as a proton conductor for high temperature operation of DMFC. At 80℃, the open-circuit-voltage (OCV) was increased from 0.722V (PtRu/C) to 0.755V (PtRu/C-ZSM-5) and the single cell performance using the ZSM-5-PtRu/C of MEA at 0.4V showed 180mA/cm^2 at 140℃. Whereas DMFC operation with PtRu/C anode, it is not possible to operate above 120℃. Figure 4 shows impedance spectra of DMFC anode. The membrane resistance and interfacial resistance decreased by the addition of the zeolite(ZSM-5) in all range of operating temperature. The membrane resistance and interfacial resistance obtained impedance spectra at 120℃. From these result, we can suggest that zeolite(ZSM-5) helps to operate DMFC at higher temperature and also helps the membrane to mobile protons.

4. Conclusions

ZSM-5 was added to PtRu/C electrode to improve the performance of direct methanol fuel cell. Through the high-throughput-screening test, the catalysts composed of PtRu : ZSM-5 = 7 : 3 were most active in electro-oxidation of methanol. The addition of ZSM-5 to PtRu/C, impedance the thermal stability oh DMFC operation. The DMFC performance was also improved by addition of ZSM-5 to PtRu/C electrode. The membrane resistance and interfacial resistance decreased by the addition of the zeolite(ZSM-5) in all range of operating temperature.

Reference

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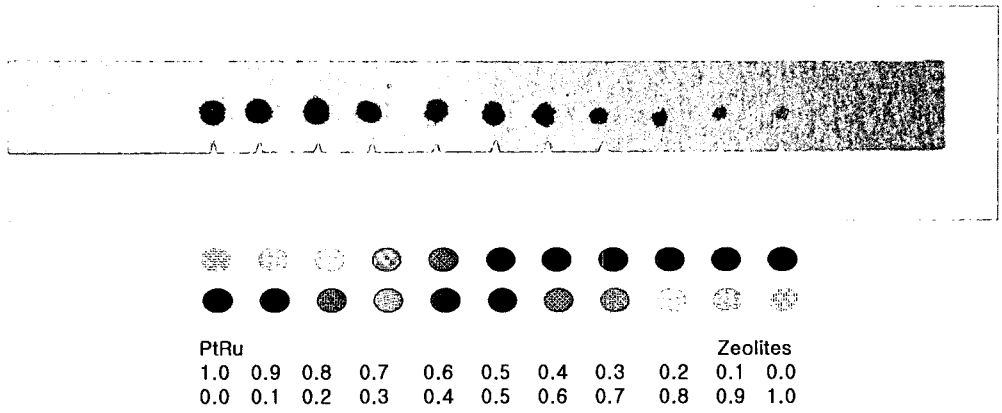


Fig. 1. The array of PtRu and zeolite(ZSM-5) for high-throughput-screening test.

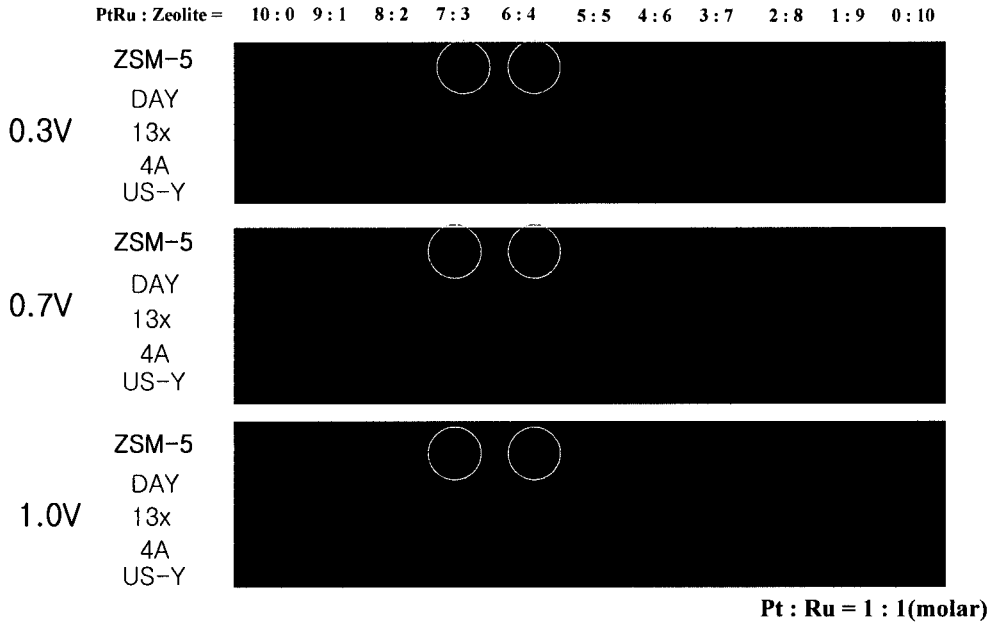
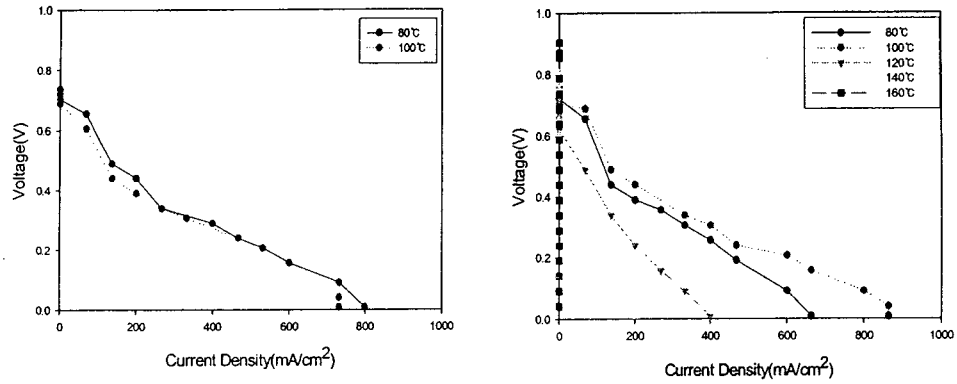
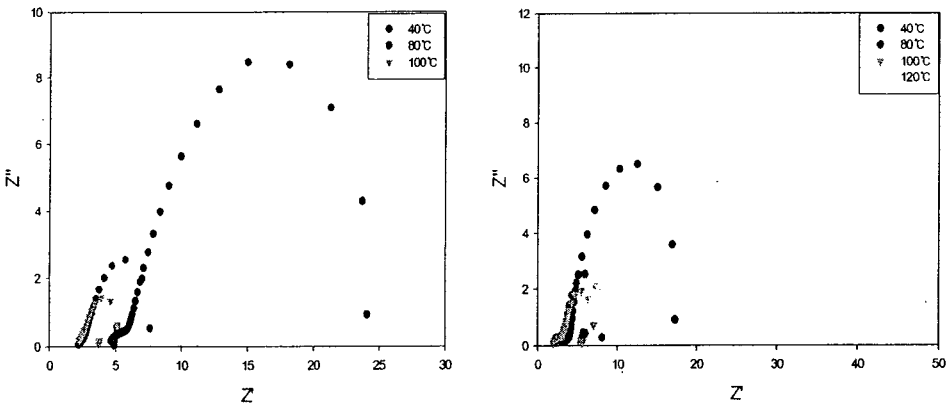


Fig. 2. High-throughput-screening test array results by fluorescence imaging.



(a) (b)

Fig. 3. Comparison of the single cell performance at the temperature using the prepared Anode (a) = PtRu/C, (b) = PtRu/C-zeolite(ZSM-5)



(a) (b)

Fig. 4. Comparison of the impedance spectra at the temperature using the prepared Anode (a) = PtRu/C, (b) = PtRu/C-zeolite(ZSM-5)