



^{195}Pt NMR Study of the Influence of Nafion Ionomer on the Enhanced Local Density of States at the Surface of Carbon-Supported Pt Catalysts

Kee Sung Han¹ and Moohee Lee^{2*}

¹Daegu Center, Korea Basic Science Institute, Daegu 702-701, Republic of Korea

²Department of Physics, Konkuk University, Seoul 143-701, Republic of Korea

Abstract : ^{195}Pt NMR measurements were performed to deduce the variation of local density of states at the Fermi energy (E_F -LDOS) at the surface of carbon-supported Pt catalysts due to the addition of Nafion[®] ionomer in the metal-electrode-assembly for fuel cells. The results showed that the E_F -LDOS at the surface of Pt particles was enhanced by the addition of Nafion[®] ionomers whereas it was uninfluenced in the inner (bulk) part of the Pt particles. This suggests that the effects of ionomers on the electronic states of the Pt particle surface are related to the electrochemical activity of the catalysts.

Keywords : ^{195}Pt NMR, Pt Catalysts, Nafion ionomer

INTRODUCTION

The electronic states at the surface of Pt catalysts are closely related to the catalytic activities of Pt particles in fuel cells¹⁻⁶. Those states can be easily influenced by several things such as supporting materials and alloying metals to promote the catalytic activities of platinum particles via so-called metal-support interactions and ligand effects¹⁻¹¹. A number of nuclear magnetic resonance (NMR) spectroscopy reports have been published regarding the electronic states, namely the local density of states at the Fermi level (E_F -LDOS), of Pt catalysts by measuring ^{195}Pt NMR and ^{13}C NMR of CO adsorbed on the surface of Pt particles¹⁻¹³. These NMR measurements, in conjunction with electrochemical measurements such as cyclic voltammetry¹⁴ and chrono-amperometry¹⁴, are utilized to find

* To whom correspondence should be addressed. E-mail : mhlee@konkuk.ac.kr

out the catalytic activities of commercial and/or model catalysts as well as the oxidation of methanol and/or CO for application in direct methanol fuel cells (DMFC). The DMFC is one of the optimum candidates for an alternative power source of portable gadgets and small transportations^{15,16}. The core of a DMFC is the membrane-electrode-assembly (MEA), which consists of an anode, a proton exchange membrane and a cathode. The anode and the cathode are covered with catalysts and mixed with ionomers. Ionomers are added for MEA binding and generation of proton conducting path^{15,17,18}. Nafion[®] and Nafion[®] ionomers are widely used as, respectively, a proton exchange membrane and a common ingredient. Therefore the performance of DMFCs strongly depends on the extent of catalysts/ionomer and fabrication methods of MEA^{17,18}. In addition, the reduction of CO oxidation in a MEA¹⁹ and the production of H₂O₂¹¹ in the fuel reaction are crucial.

In this work we performed ¹⁹⁵Pt NMR of Pt catalysts supported on carbon (Pt/C) to deduce the influence of Nafon[®] ionomers on the electronic states of the Pt particles in the MEA. Our results show that the E_F-LDOS at the surface of Pt particles is enhanced by the addition of Nafion[®] ionomers whereas the bulk part of Pt particles is uninfluenced.

EXPERIMENTAL

The MEA was made by hot-pressing pre-treated Nafion 117[®] (Dupont, USA) as a PEM between both electrodes with the pressure of 100 kg/cm² at 130 °C for 3 minutes. The electrodes consisted of carbon cloth (E-Tek, USA) diffusion layer coated with carbon black backing layers and catalysts; 60% Pt on Vulcan XC-72 (Pt/C) electro-catalysts (E-Tek, USA). The catalyst inks, for which the ratio in wt % of Nafion[®] ionomer to the electro-catalysts was 0.1:1, were prepared with 5 wt % Nafion[®] ionomer solution (Aldrich, USA) and then sprayed onto the backing layer of carbon clothes (4×2 cm²) up to the amount of 5 mg Pt/cm² by using N₂ gas. Therefore the total amount of catalysts was 80 mg. More detailed protocol of MEA fabrication can be found in the references²⁰. For interpretational convenience of ¹⁹⁵Pt NMR data, the fabricated MEA prepared by using Pt/C mixed with the Nafion ionomer is denoted as Pt/C-NI, whereas that prepared with Pt/C catalyst only (without the Nafion ionomer) is denoted as Pt/C-noNI.

The ¹⁹⁵Pt NMR experiments were carried out with a home-made spectrometer and a home-made probe in an 8 T superconducting magnet (Oxford, UK) at the temperature range of 10 ~ 80 K. The ¹⁹⁵Pt NMR spectra were obtained by point-by-point method by using spin-echo pulse sequence ($\pi/2-\tau_0-\pi-\tau_0$ -acquire) with a 0.001 kG/MHz (~63 kHz) difference between each echo signal positions at 20 K. Typical length of 90 degree pulse was 10 μ s. Spin-lattice relaxation T_1 was measured at both the surface peak position, 1.100 kG/MHz, and the bulk peak position, 1.134 kG/MHz, by a saturation-comb pulse sequence ²¹ at various temperatures.

RESULTS AND DISCUSSION

The ¹⁹⁵Pt NMR spectra of the Pt/C-NI and the Pt/C-noNI were obtained at 20 K and presented in Fig. 1. The ¹⁹⁵Pt NMR spectra showed a typical spectral shape of nano-sized Pt particles. The layer model analysis of the ¹⁹⁵Pt NMR spectrum is well established and it makes possible to distinguish where the peak comes from in the particles according to a resonance position ^{1-6,9,11,12}. The peak at 1.089 kG/MHz comes from Pt-oxides ^{1,9,12,13}. The maximum of the bulk peak shifts from 1.138 kG/MHz to lower field of 1.1195 kG/MHz ¹² and about 1.13 kG/MHz ¹², which is at 1.134 kG/MHz in our samples, due to the perturbation of surface atoms to interior atoms ². The surface peak is diminished at the position of 1.092 kG/MHz and the Pt-oxide peak appears at 1.089 kG/MHz in the Pt/C-noNI. However, the Pt/C-NI shows another peak at the position of 1.092 kG./MHz due to the addition of the Nafion ionomer. This means that Nafion ionomer can influence the surface states of Pt particles like other adsorbates, which show induced peaks at various positions proportional to the electro-negativities of the adsorbates ¹⁻⁹. The spin-lattice relaxation rate, $1/T_1$, measured at both the surface (1.100 kG/MHz) and the bulk (1.134 kG/MHz) peak positions at various temperatures were shown in the inset of Fig. 1. The decays of spin-lattice relaxation were single-exponential in the bulk and the surface peak positions at all measured temperatures for both samples, as plotted in Fig. 2.

The temperature dependence of $1/T_1$ shows a straight line, $1/T_1 \sim T$, confirming the Korringa relationship ($T_1 T = \text{constant}$), which is a NMR fingerprint of metallic states, at

both the bulk and the surface peak positions for both the Pt/C-NI and the Pt/C-noNI. While the slopes of the straight lines obtained at the bulk position (1.134 kG/MHz) are the same, the larger slope in the Pt/C-NI than in the Pt/C-noNI at the surface position (1.100 kG/MHz) suggests enhancement of E_F -LDOS at the surface of Pt particles in the Pt/C-NI. Typical T_1T values for ^{195}Pt NMR of Pt particles at the bulk position (1.134 kG/MHz) and even at 1.1195 kG/MHz¹², far from a typical bulk position (1.138 kG/MHz), are about $30 \pm 1 \text{ ms} \cdot \text{K}$ ^{12,13,22}. Those values at the surface position (1.100 kG/MHz) are about $49 \sim 52 \pm 3 \text{ ms} \cdot \text{K}$ in the clean Pt surfaces^{2,12} and $81 \pm 4 \text{ ms} \cdot \text{K}$ in the untreated Pt surfaces¹³, which are covered with Pt-oxides. Our T_1T values of $24 \pm 3 \text{ ms} \cdot \text{K}$ for both the Pt/C-NI and the Pt/C-noNI at the bulk position are close to the typical values of the bulk Pt atoms. In addition, the T_1T value of $80 \pm 5 \text{ ms} \cdot \text{K}$ in the surface of the Pt/C-noNI is the same as that of the untreated surface of Pt particles¹³. However, the T_1T value at the surface of the Pt/C-NI is reduced to $60 \pm 4 \text{ ms} \cdot \text{K}$. This clearly confirms that the Nafion ionomer shortens T_1 and reduces T_1T by enhancing E_F -LDOS of the surface of Pt particles, in contrast to the Pt/Pd coated with polymers⁵. Although it is controversial whether the catalytic activity to methanol and CO oxidation increases¹⁻⁴ or decreases⁶ with E_F -LDOS of Pt particles, it is believed that the catalytic activities of Pt are strongly related to the E_F -LDOS at the surface of Pt particles. Therefore, it is possible that the Nafion ionomer acts as not only a MEA binder and a proton conductor but also a modifier of the catalytic activity of the catalysts during electro-chemical reaction and fuel operation.

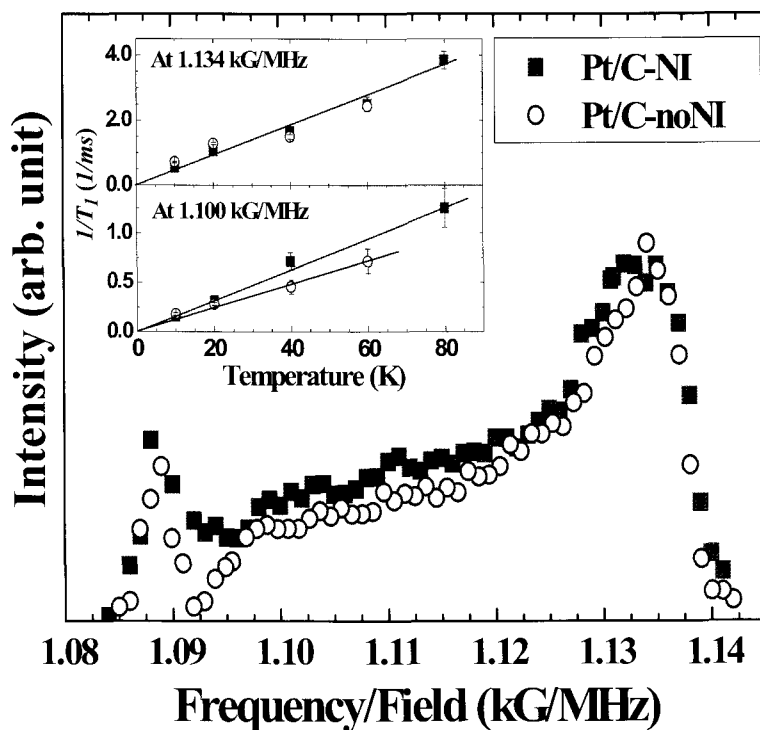
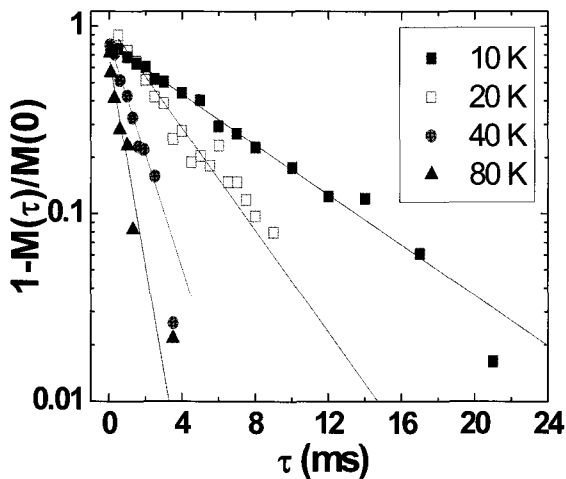


Fig. 1. ¹⁹⁵Pt NMR spectra of commercial 60% Pt/C in the membrane electrode assemblies (MEAs) fabricated with Nafion ionomer (Pt/C-NI) and without Nafion ionomer (Pt/C-noNI) obtained at 20 K and 8 T. The spectrum of the Pt/C-NI shows an enhanced peak at 1.092 kG/MHz due to the addition of Nafion ionomer. The inset shows temperature dependences of $1/T_1$ at the surface (1.100 kG/MHz) and the bulk (1.134 kG./MHz) peak positions. The larger slope confirms an increase of E_F -LDOS. The lines are guide to the eyes.

(a) At Surface (1.100 kG/MHz) of Pt/C-NI



(b) At Bulk (1.134 kG/MHz) of Pt/C-NI

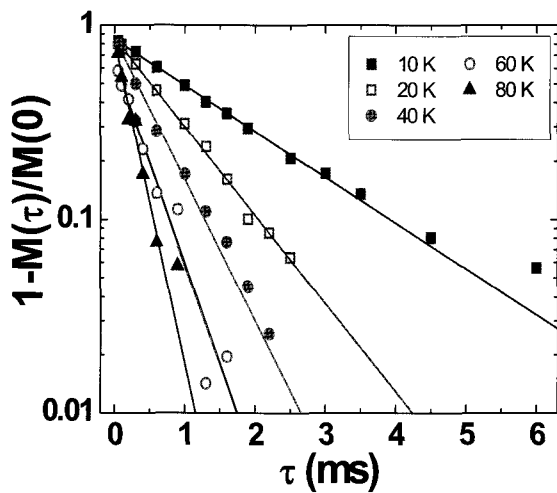


Fig. 2. The spin-lattice relaxation recovery obtained at the surface (1.100 kG/MHz) (a) and the bulk (1.134 kG/MHz) (b) peak positions of the Pt/C-NI at various temperatures. It shows a single-exponential decay at all measured temperatures.

CONCLUSION

In summary, MEA fabrication and Nafion ionomer effects on the electronic states in the Pt catalyst surface have been studied by using ¹⁹⁵Pt NMR measurements. The E_F-LDOS at the Pt nano-particle surface is enhanced by addition of Nafion ionomer. Therefore, the modification of the electronic states at the Pt particle surface due to the addition of proton conducting ionomer should be considered and utilized in the design of Pt catalysts and in the development of proton exchange membranes. Also it is important to investigate the modification of electronic states at the Pt particle surface in fabricated MEAs with other proton exchange membrane materials to order to find out new insights into the relation between catalysts and proton conductors for better performance of fuel cells.

REFERENCES

1. P. K. Babu, Y. Y. Tong, H. S. Kim, A. Wieckowski, *J. Electroanal. Chem.* **157**, 524-525 (2002)
2. P. K. Babu, H. S. Kim, E. Oldfield, A. Wieckowski, *J. Phys. Chem.* **107**, 7595-7600 (2003)
3. P. K. Babu, H. Kim, S. T. Kuk, J. H. Chung, E. Oldfield, A. Wieckowski, *J. Phys. Chem. B* **109**, 17192-17196 (2005)
4. Y. Tong, H. S. Kim, P. K. Babu, P. Waszuk, A. Wieckowski, E. Oldfield, *J. Am. Chem. Soc.* **124**, 468-473 (2002)
5. Y. Y. Tong, T. Yonezawa, N. Toshima, J. J. van der Klink, *J. Phys. Chem.* **100**, 730-733 (1996)
6. F. Tan, B. Du, A. L. Danberry, I.-S. Park, Y.-E. Sung, Y. U. Tong, *Faraday Discuss.* **140**, 139-153 (2008)
7. K. S. Han, P. K. Babu, O. H. Han, *J. Electrochem. Soc.* **152**, J131-J135 (2005) and references therein.
8. K. S. Han, Y.-S. Moon, O. H. Han, K. J. Hwang, I. Kim and H. Kim, *Electrochem. Commun.* **9**, 317-324 (2007) and references therein.

9. P. K. Babu, E. Oldfield, A. Wieckowski, *Mordern Aspects of Electrochemistry* 36, eds. C. G. Vayenas, B. E. Conway, and R. E. White, *Kluwer Academic/Plenum Publishers, New York* **1**, 1-50 (2003)
10. J. J. Van der Klink, *Advnaces in Catalysis* 44, eds. W. O. Haag, B. C. Gates, and H. Knozinger, *Academic Press, New York* **1**, 1-117 (2000)
11. H. Yano, J. Inukai, H. Uchida, M. Watanabe, P. K. Babu, T. Kobayashi, J. H. Chung, E. Oldfield, A. Wieckowski, *Phys. Chem. Chem. Phys.* **8**, 4932-4939 (2006) and references therein.
12. Y. Y. Tong, C. Rice, N. Godbout, A. Wieckowski, and E. Oldfield, *J. Am. Chem. Soc.* **121**, 2996-3003 (1999)
13. C. P. Slichter, *Surf. Science* **106**, 382-396 (1981)
14. A. J. Bard, L. R. Faulkner, *Electrochemical Methods-Fundamentals and Applications*, *John Wiley & Sons, New York* (1980)
15. L. Carrette, K. A. Friedrich, U. Stimming, *Fuel Cells* **1**, 5-39 (2001)
16. A. S. Arico, S. Srinivasan, V. Antonucci, *Fuel Cells* **1**, 133-161 (2001)
17. M. P. Hogarth, T. R. Ralph, *Platinum Metals Rev.* **46**, 146-164 (2002)
18. B. Krishnamurthy, S. Deepalochani, K. S. Dhathathreyan, *Fuel Cells* **8**, 404-409 (2008)
19. I. Tkach, A. Panchenko, T. Kaz, V. Bogel, K. A. Friedrich, E. Roduner, *Phys. Chem. Chem. Phys.* **6**, 5419-5426 (2004)
20. K. Sundmacher, T. Schultz, S. Zhou, K. Scott, M. Ginkel, and E. D. Gilles, *Chem. Eng. Sci.* **56**, 333-341 (2001) and reference therein.
22. E. Fukushima, and S. B. W. Roeder, *Experimental Pulse NMR*, Addison-Wesley, Reading, Massachusetts, 174-176 (1981)
23. W. P. Halperin, *Rev. Mod. Phys.* **58**, 533-603 (1986)