

# Synthesis of Metal Oxide Nanoparticles in Restricted Space of Perfluorosulfonate Ionomeric Membrane: Nafion<sup>®</sup>

Shigehito DEKI<sup>1</sup>, Takashi HASEGAWA<sup>2</sup> and Minoru MIZUHATA<sup>2</sup>

<sup>1</sup> Professor Emeritus, Kobe University

<sup>2</sup> Department of Chemical Science and Engineering, Graduate School of Engineering, Kobe University, 1-1, Rokkodai-cho, Nada, Kobe 657-8501, Japan

E-mail : deki@kobe-u.ac.jp, hasegawa@cx2.scitec.kobe-u.ac.jp, mizuhata@kobe-u.ac.jp

It is well-known that metal oxide dispersed Nafion membrane is utilized for the non-humidified fuel cell by the improvement of water uptake performance<sup>1)</sup>. Several research has been attempted for the improvement of the fuel cell performance. However, casted membrane has used in most studies because the metal oxide cannot be mixed with the nafion membrane and used Nafion solution for mixing with the oxide particle and ion-exchange polymer. On the other hand, it is known that the ion channel exists for ionic conduction in the Nafion membrane, so-called "cluster structure" named by Yeager<sup>2)</sup> and Gierke<sup>3)</sup> for Nafion membrane. The Nafion membrane in water media with large ion exchanging capacity (ca. 1.0 meq/g) is known the existence of ionic cluster contributed from nanophase segregation of hydrophobic-hydrophilic region. In order to discuss the structural properties of the nafion/ metal oxide composite, it is better to use the uniform membrane containing the metal oxide. We have been studied the fabrication of metal oxide/ organic compound composite using the Liquid Phase Deposition which is one of the preparation method of metal oxide called *soft solution process*<sup>4)-6)</sup>. The dye/TiO<sub>2</sub> composite<sup>4)</sup> and protein templated hybrid materials for biosensing<sup>5)</sup> has been obtained. The mechanism is considered ligand exchanging hydrolysis of metalfluoro complex and F<sup>-</sup> consumption reaction for accelerate of metal oxide's supersaturation. In this study, we prepare the TiO<sub>2</sub> nanoparticles in perfluorosulfonate ionomeric membrane (Nafion<sup>®</sup> by DuPont) using the LPD method. Using this method, we also fabricated the TiO<sub>2</sub>:Eu<sup>3+</sup> nanoparticle dispersed in Nafion membrane. In this system, we measure the photo luminescence of Eu<sup>3+</sup> doped in metal oxide nanopertilces for evaluating an enhancement of photo luminescence intensity.

We confirmed the deposition of TiO<sub>2</sub> nanoparticles in Nafion membrane after immersion into the mixed aqueous solution of metalfluoro complex and boric acid. The size of nanoparticles is narrow distribution and the particles is TiO<sub>2</sub> anatase assigned from SAED pattern and lattice space of (101) 3.5 Å. From depth profile of Ti XPS spectra, the existence of Ti can be confirmed in ca. 10 μm depth.

Photo luminescence (PL) spectrum of Nafion / TiO<sub>2</sub>:Eu<sup>3+</sup> is an effective way to investigate the electronic structure and optic characteristics of semiconductor nano-materials, by which the information such as surface oxygen vacancies and defects as well as separation and recombination of charge carriers can be obtained. Figure is TEM image of nanoparticles in Eu<sup>3+</sup> Nafion and inset shows the PL excited by 398 nm (Eu<sup>3+</sup> : <sup>7</sup>F<sub>0</sub>→<sup>5</sup>D<sub>4</sub>). Nanoparticles are TiO<sub>2</sub> anatase assigned from SAED. From the emission spectra, it can be observed that the most intense peak around 595 nm, which corresponds to the magnetic dipole transition between the <sup>5</sup>D<sub>0</sub> and <sup>7</sup>F<sub>1</sub> levels and is much stronger than that of the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> transition. It is well-known that the selection rules and transition probabilities between states strongly depend on the crystal field<sup>7, 8)</sup>. If the Eu<sup>3+</sup> ions embedded in a site with inversion symmetry, the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>1</sub> magnetic dipole transition is dominating, while in a site without inversion symmetry the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> electric dipole transition is the strongest contributed from their parity. In this spectra, The emission intensity at 617 nm (<sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub>) is enhanced by inducing TiO<sub>2</sub>. Inducing TiO<sub>2</sub> nanoparticles cause changing the symmetry of Eu<sup>3+</sup> crystal field.

This study was partly supported by Grant-in-Aid for Scientific Research (A)(No. 19205029), by Grant-in-Aid from MEXT, Japan.

## References

- 1) M. Watanabe, H. Uchida, Y. Seki, M. Emori, *J. Electrochem. Soc.*, **143**, 3847 (1996).
- 2) H.L. Yeager and A. Steck, *J. Electrochem. Soc.*, **128**, 1880, 1981.
- 3) T. D. Gierke, G. E. Munn, F. C. Wilson, *J. Poly. Sci; Poly. Phys. Edit.* **19**, 1687 (1981).
- 4) S. Deki, Y. Kodama, M. Mizuhata, *J. Ceram. Soc. Jpn*, **117**, 326 (2009).
- 5) M. Tatemichi, M. Sakamoto, M. Mizuhata, S. Deki, T. Takeuchi, *J. Am. Chem. Soc.*, **129**, 10906 (2007).
- 6) L. Li, M. Mizuhata, A. Kajinami, S. Deki, *Synthetic Metals*, **146**, (14), 17, (2004).
- 7) B. R. Judd, *Phys. Rev.* **127**, 750 (1962).
- 8) G. S. Ofelt, *J. Chem. Phys.* **37**, 511 (1962).

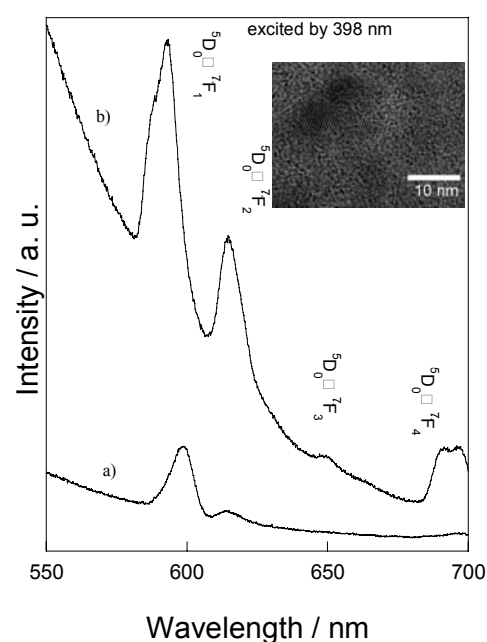


Fig.1. Emission spectra excited by 396 nm (<sup>7</sup>F<sub>0</sub>→<sup>5</sup>D<sub>4</sub>) of Eu<sup>3+</sup>-Nafion before<sup>a)</sup> / after<sup>b)</sup> deposition of TiO<sub>2</sub>. Inset shows TEM image of nanoparticle in Eu<sup>3+</sup>Nafion. The lattice space TiO<sub>2</sub> anatase (101) was visible.