



Luminescent Polymer Electrolyte Composites Using Silica Coated- $Y_2O_3:Eu$ as Fillers

Mikrajuddin Abdullah¹ & Kikuo Okuyama²

¹Department of Physics, Bandung Institute of Technology
Jl. Ganeca 10 Bandung 40132, Indonesia
E-mail: din@hiroshima-u.ac.jp

²Department of Chemical Engineering,
Graduate School of Engineering, Hiroshima University,
1-4-1 Kagamiyama, Higashi Hiroshima 739-8527, Japan

Abstract Luminescent polymer electrolyte composites composed of silica coated $Y_2O_3:Eu$ in polyethylene glycol (PEG) matrix has been produced by initially synthesizing silica coated $Y_2O_3:Eu$ and mixing with polyethylene glycol in a lithium salt solution. High luminescence intensity at round 600 nm contributed by electron transitions in Eu^{3+} ($^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$, and $^5D_0 \rightarrow ^7F_3$ transitions) were observed. The measured electrical conductivity was comparable to that reported for polymer electrolyte composites prepared using passive fillers (non luminescent). This approach is therefore promising for production of high intensity luminescent polymer electrolyte composites for use in development of hybrid battery/display.

Keywords: *luminescence spectra; polyethylene glycol; europium doped-yttria ($Y_2O_3:Eu$); electrical conductivity.*

1 Introduction

We have reported the synthesis and characterization of luminescence polymer electrolyte nanocomposites in which nanoparticles serve as luminescence center (polyethylene glycol and zinc oxide nanoparticles) [1-3]. In the future, those composites could have potential application for making hybrid battery-display or fuel cell-display, i.e., combination of battery or fuel cell and display in a single device. However, the ZnO based luminescent polymer electrolyte [1,2] or europium doped-ZnO [3] we made previously showed relatively weak luminescence intensity so that still not available for industrial applications.

Rare earth ions have long been used for producing phosphor materials [4,5]. Doping appropriate host matrix (usually oxide) with those ions produces sharp and intense emission under ultraviolet excitation. It is then interesting to investigate the potential use of rare ions doped oxide nanoparticles as filler in making polymer electrolyte composites to produce high emission intensity.

Since polymer electrolyte contains reactive ions (usually alkali), and possibly some chemical reactions might occur during storage or operation time, those nanoparticles must be protected from their surrounding to avoid the change of luminescence intensity (degradation). Coating those nanoparticles with inert materials is a possible choice. Coating of $Y_2O_3:Eu$ nanoparticles with silica, which produces red emission, has been reported by Cannas et al [6] using gel method. However, this method produced large grain size glass, although the presence of nanometer sized $Y_2O_3:Eu$ in glass was confirmed to appear. This morphology is not suitable for use as filler in polymer electrolyte since the grain size is too large.

We modify this method by adding large amount of alkali salt prior to drying. The large amount of alkali salt prevents the agglomeration of born-nuclei so that each nuclei will be surrounded by salt and reduce the tendency of making contacts with another nuclei [7]. By heating, each nucleus is still separated from the others so that the size growth can be avoided. After heating, the material is then washed with water several times (combined with centrifugation) to remove the salt and resulting separated silica-coated $Y_3O_3:Eu$.

It was found that the conductivity of electrolyte changes with operation time or storage time [8]. During the operation of batteries or fuel cells, the properties of the electrolyte, such as conductivity, might change. The luminescence intensity must be resist to the change of the properties of electrolyte. In the previous reports, the effect of conductivity change on the luminescence of composite has not been investigated. The objectives of this work are synthesizing micrometer sized europium doped particles by a simple method, the use of the particles to produce polymer electrolyte composite and investigating the luminescence intensities of the composites when the conductivity of electrolyte fluctuates during aging or operating time.

2 Theoretical Inspections

The presence of conductivity lead to the attenuation of electromagnetic wave to result a reduction in the intensity, according to

$$I_l \propto \exp(-\alpha z), \quad (1)$$

with $\alpha = 2n_l \omega / c$, is the absorption coefficient, ω , c , and z are frequency, the speed of light in vacuum, and the distance passed by light, and n_l is the imaginary part of refraction index, given by [9]

$$n_I = \sqrt{\varepsilon} \left[\frac{1}{2} \sqrt{1 + \left(\frac{4\pi\sigma}{\varepsilon\varepsilon_0\omega} \right)^2} - \frac{1}{2} \right]^{1/2} \quad (2)$$

with ε dielectric constant, ε_0 the electrical permittivity of vacuum, and σ the electrical conductivity. For polymer electrolyte, the conductivity is usually smaller than 1 S/m so that $4\pi\sigma/\varepsilon_0\omega < 0.0014$. This gives

$$n_I \approx (1/2\sqrt{\varepsilon})(4\pi\sigma/\varepsilon_0\omega) \text{ and } \alpha \approx \frac{\omega}{c\sqrt{\varepsilon}} \left(\frac{4\pi\sigma}{\varepsilon_0\omega} \right) \quad (3)$$

Using $\sigma \approx 1$ S/m (the maximum reported electrical conductivity), and $\varepsilon \approx 2.2$ belongs to most of polyethylene based-polymers [10], one find $\alpha \approx 3.2 \times 10^3 \text{ m}^{-1}$. This means that, the reduction of intensity by a factor of $1/e$ occurs when the wave traveled a distance of about $z = 1/\alpha \approx 0.3$ mm. For most reported polymer electrolyte with conductivity smaller than 1 S/m, the absorption is much smaller and the attenuation of light can be ignored. In other words, the effect of electrolyte conductivity fluctuation on the luminescence intensity can be ignored if the film thickness is less than several hundreds of micrometer. This prediction will be compared with experimental data.

3 Experiment

Similar to that reported by Cannas et al [6], Eu(NO₃)₃.6H₂O (Kanto Chemicals) 0.1175 g and Y(NO₃)₃.6H₂O (Kanto Chemicals) 0.8625 g were dissolved in 8 mL ultra pure water. Tetraethyl orthosilicate (TEOS, Kanto Chemicals) 8.7 g was dissolved in 8 mL ethanol. Two mixtures were then mixed and left for 30 min. Two LiCl solutions in water: 1 g and 3 g, each in 20 mL ultra pure water were made. Each salt solution was mixed with 10 mL Y/Eu/TEOS solution and then dried at 60 °C until all solvent evaporated and obtaining silica compound. Another Y/Eu/TEOS mixture was dried without mixing with salt. The samples were then heated at 800 °C for 4 hours. A fraction of samples with salts were then washed with ultra pure water in ultrasonic bath to remove salt and centrifuged. To optimize the washing repetition, we measured the electrical conductivity of sample after ultrasonic treatment. We found the electrical conductivities after three times and four times washing were nearly similar. We then concluded that no further salt was found in the sample and four times washing was enough to remove all salt. Finally the samples were then dried and characterized.

Polymer electrolyte composites were made by dissolving 0.048 LiCl in 50 mL ultra pure water followed by addition of 0.5 g polyethylene glycol 2,000,000 (Wako Pure Chemicals). The molar fraction of Li ions with respect to the ethylene glycol unit was around 10%. In this mixture, 20 wt.% of powder was dispersed, followed by mixing using magnetic stirrer and ultrasonic bath and dried at 60 °C until all solvent evaporates.

The XRD patterns were recorded using Rigaku Denki RINT2000 (CuK α source). The electrical conductivities were measured using Precision LCR Meter Agilent HP4284H. For measuring the electrical conductivity, the samples were pressed between two stainless steel electrodes. Luminescence spectra were measured using Shimadzu Photometer RF-5300PC. Scanning electron micrograph pictures were recorded using Field Emission SEM Hitachi S5000.

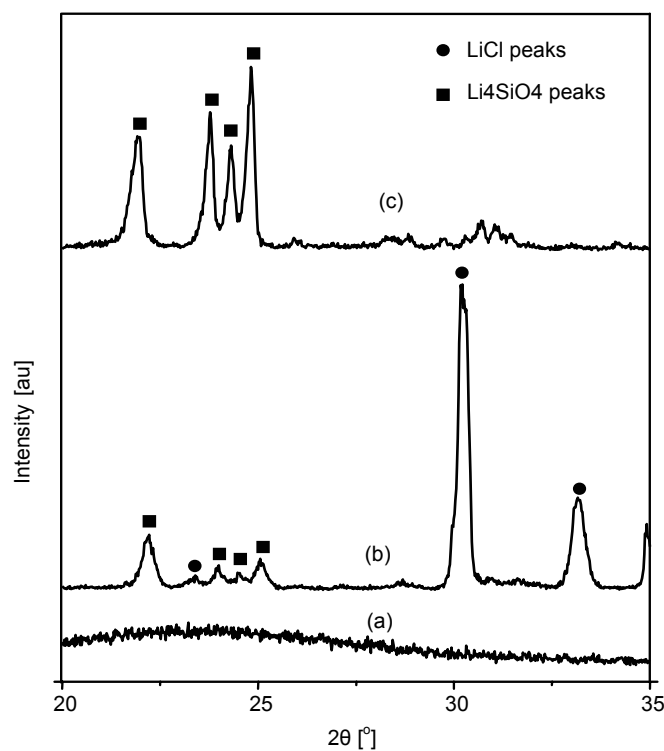


Figure 1 (a) XRD patterns of sample prepared without salt after heating. (b) XRD patterns of sample prepared with salt after heating, but prior to washing. (c) XRD patterns of sample prepared with salt after heating and washing.

4 Results and Discussion

We prepared the samples with salt and without salt. Without salt, large grain glass particles up to one centimeter sizes were found. This size is unsuitable for use as filler in polymer composite. Before characterizations this sample was crushed to form fine powder. XRD patterns as shown in Fig. 1(a) indicated that the heated sample prepared without salt appeared in amorphous state. No peak of yttria or europium oxide was observed in the patterns. We have also tried another heating temperatures up to 1000 °C (the upper limit of our heater), and no significant change in the XRD patterns was observed (still appeared in amorphous state). This observation was possibly due to the use of small amount of these materials compared to silica. The heated sample produced using salt shows XRD peak as in Fig. 1(b) in which the domination of LiCl peak was observed incorporating with weak additional peaks. The washed sample shows XRD pattern as in Fig. 1(c) in which LiCl peak disappeared and addition peaks observed in curve (b) became dominant. It indicated that before washing, large amount of LiCl was found around which then dissolve during washing. The peak in Fig. 1(c) can be identified as Li₄SiO₄ (monoclinic), correspond to $\langle \bar{1}00 \rangle$, $\langle 011 \rangle$, $\langle \bar{1}01 \rangle$, and $\langle 101 \rangle$ reflections (JCPDS 37-1472). The presence of lithium silicate was due to the diffusion of lithium ions into silicate during heating. There are other reports that the use of filler containing alkali ions can enhance the conductivity.

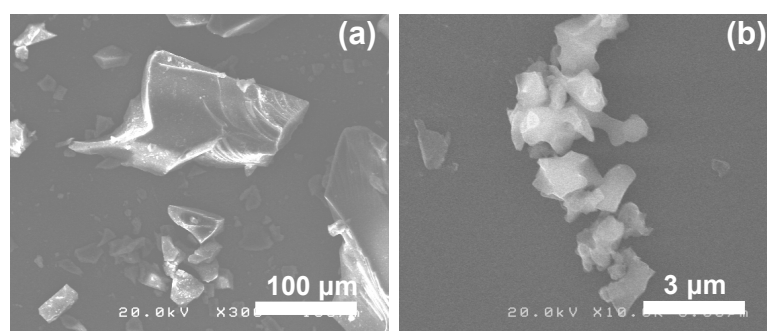


Figure 2 SEM pictures of samples prepared without salt (a) and with salt (b).

SEM picture of grounded sample prepared without salt and ungrounded sample prepared with salt are displayed in Fig. 2. The sample prepared with salt have grain size about one micrometer, very small compared to the sample prepared without salt of about one centimeter size prior to crushing. This size is enough for use in developing polymer electrolyte composites. The ranges of particle sizes used to make polymer electrolyte composites are between several nanometer up to about ten micrometer [11].

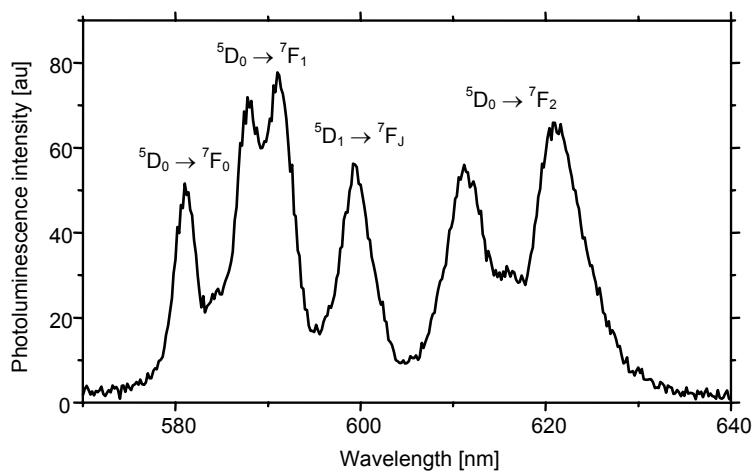


Figure 3 Photoluminescence emission of samples excited using a wavelength of 254 nm.

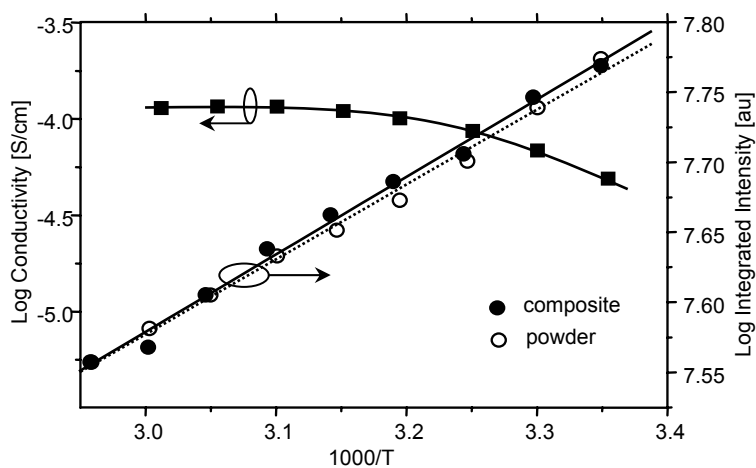


Figure 4 Solid square, the effect of temperature on the electrical conductivity of polymer electrolyte composites. Solid circle, the effect of temperature on the integrated luminescence intensity of polymer electrolyte composite sample. Open circle, the effect of temperature on the integrated luminescence intensity of filler only.

Figure 3 shows the luminescence spectrum of coated $\text{Y}_2\text{O}_3:\text{Eu}$ materials detected at 25.5 °C. The spectrum shows peaks ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$, and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$ transitions [5]. The peak at 600 nm is probably contributed by ${}^5\text{D}_1 \rightarrow {}^7\text{F}_J$ transition. Using a handy UV source, the red color of composite can be observed clearly at room illumination background. The intensity was very high

compared to that our previous reports for ZnO-based composite. We believe such a high luminescence intensity is ready for use in industry, for example to develop a hybrid battery/display, i.e., a battery and a display that integrated in a single device. The presence of several peaks was due to the amorphous state of Y₂O₃. For crystalline Y₂O₃ host, the 612 nm peak dominates another peaks [5].

Electrical conductivity as a function of temperature of sample prepared using 8 mol. % salt is displayed in Fig. 4 (solid square). This shape is typical of conductivity of polymer electrolyte composites, i.e., has a Vogel-Tamman-Fulcher profile [1,2]. The highest electrical conductivity observed at around melting point was 10⁻⁴ S/cm, so that the absorption coefficient is $\alpha \approx 30 \text{ m}^{-1}$.

To confirm that the intensity of the composite is unaffected by the change of electrolyte conductivity, we measured the effect of temperature change from room temperature up to the melting point of polymer on the luminescence intensity. Solid circle in Fig. 4 is the temperature dependence of integrated intensity, defined as

$$I_T = \int_{575 \text{ nm}}^{640 \text{ nm}} I(\lambda) d\lambda$$

with $I(\lambda)$ is the measured intensity. The boundary of integration was fixed to these above values since only background signal was observed outside this range. The integrated intensity decreased with increasing temperature. We also measured similar change in the intensity for powder only (open circle in Fig.4), showed exactly similar trends. Different in the value was due to the different in the background of composite film and powder sample. These results indicated that the change in the intensity was contributed by fillers, instead of the change in the electrolyte conductivity. The effect of temperature on the excitation spectra of Eu-doped oxide has been reported previously [5]. We also prepared samples using different salt concentrations: 5 mol.%, 10 mol.%, 20 mol.%, and 40 mol.%. The luminescence intensity was found to be independent on the salt concentration. This result indicated that even there is a change or fluctuation in the conductivity of electrolytes, the luminescence intensity does not change if temperature is constant.

The thickness of film composite used in the experiment was less than 0.1 mm. With coefficient of absorption about 30 m⁻¹, the reduction in the intensity after light traveled the film thickness was only about 0.3%.

5 Summary

Luminescent polymer electrolyte composites have been made using silica coated-Y₂O₃:Eu as filler to produce intense red luminescence around 600 nm. The fillers were initially synthesized by mixing silica and Y₂O₃:Eu precursors, adding specified amount of salt and heating at 800 °C. After heating, the added salt dispersed inside the particle and broke the particle into smaller grains when washed in an ultrasonic bath (the salt dissolved). The luminescence intensity was observed to be independent on the conductivity of the electrolytes, which places this material as a promising candidate form developing a hybrid of battery/display.

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