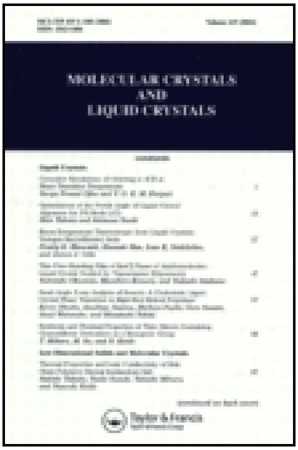

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Development of Electrode for Organic EL Materials by Cyclic Voltammetry

Don Soo Choi[a], Young Kwan Kim[a] & Ju Won Lee[a]

[a] Dept. of Chem. Eng., Hong-Ik Univ., 72-1, Sangsu-Dong, Mapo-Gu, Seoul, 121-791, KOREA

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Development of Electrode for Organic EL Materials by Cyclic Voltammetry

DON SOO CHOI*, YOUNG KWAN KIM and JU WON LEE

Dept. of Chem. Eng., Hong-Ik Univ., 72–1, Sangsu-Dong, Mapo-Gu,
Seoul 121–791 KOREA

The novel cyclic voltammetric system was constructed using the Al and ITO electrode to analyze organic EL materials and the cyclic voltammetric control programs were also developed. The rubrene film was grafted on an ITO electrode and Al electrode by vacuum deposition. The three-electrode compartment electrochemical cell consisted of ITO and Al glass as the working electrode, a platinum wire as the counter electrode, and Ag/Ag$^+$ (0.1M $AgNO_3$) as the reference electrode. Comparison of the Ag/Ag$^+$ reference electrode with the SCE reference electrode showed the potential of +0.36V at 5×10^{-4}M ferrocene in 0.1M Bu_4NClO_4 with DMF. IP and EA values of rubrene were 5.48eV and 2.59eV, respectively, in 0.1M $Bu_4NClO_4$with DMF.

Keywords: cyclic voltammetry; ITO; Al; IP; EA; electroluminescence

INTRODUCTION

In recent years, organic electroluminescent devices (OELDs) have attracted a lot interest due to their applications for the flat panel display. In this case, it is very important for the OELD optimization to find out the accurate ionization potential (IP), electron affinity (EA), and bandgap (Eg). These values are usually measured by cyclic voltammerty or UPS and UV absorption spectroscopy. Cyclic voltammetry is a dynamic electrochemical method, where the potential applied to an electrochemical cell is scanned and any resulting changes in cell current are monitored to yield a cyclic voltammogram of the redox properties of the material under study.

The oxidation process corresponds to the removal of electrons from the π-

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* *E-mail: choidonsoo@yahoo.com*

band [highest occupied molecular orbital (HOMO)], whereas the reduction process corresponds to the filling of electrons to the π*-band [lowest unoccupied molecular orbital (LUMO)]. The difference between the peak potential for the oxidation and reduction provides an estimate of the HOMO-LUMO gap of the organic EL material. These electrochemically determined energy gaps are consistent with UV/vis data, falling between the onset and peak of the π-π* transition.

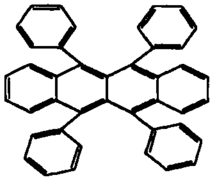

FIGURE 1. Molecular structure of rubrene.

In this paper, the electrochemical properties of rubrene was investigated with a novel cyclic voltammetric method, since rubrene was known as one of the most intensively studied organic EL materials. The molecular structure of rubrene was shown in Figure 1.

EXPERIMENTAL

The cyclic voltammograms reported here were recorded with a computer controlled system which was constructed in our laboratory. And we developed a new methodology of electrochemical analysis. We obtained the ionization potential from an ITO (indium-tin-oxide) electrode and the electron affinity from Al electrode. The ITO coated glass substrate with sheet resistance 30Ω /m^2 used as the electrode was donated from Samsung Corning Co. Ltd. Al electrode was also evaporated on grass at the pressure of 10^{-6} torr. Thin films of rubrene on an ITO electrode and Al electrode were prepared by vacuum deposition method. The thickness of rubrene on ITO and Al working electrode were 1000 Å. Rubrene layer as fabricated by the vacuum deposition from tungsten boat at a background pressure of about 10^{-8} torr, where the deposition rate was typically 0.1-0.2nm/sec.

DMF was obtained from Johnson Matthey Electronics and used as received. Bu_4NClO_4 was obtained from TCI Co. For cyclic voltammerty, an electrolyte solution of 0.1M Bu_4NClO_4 in DMF was used in all experiments. All solutions in the cell were purged with ultra-high purity N_2 for 10-15 min before each experiment. A three-electrode compartment electrochemical cell was consisted of an ITO or Al glass electrode as the working electrode in sample prepared, a platinum wire 0.6mm as the counter electrode, and Ag/Ag$^+$ (0.1M $AgNO_3$ solution with acetonitrile) as a reference electrode. The cyclic voltammograms were obtained at a scan rate of 100~20mV/sec. UV/vis absorption spectra of rubrene were obtained using a Hewlett Packard 8425A spectrometer. Photoluminescence (PL) was obtained using a Perkin Elmer LS50B in air. Thickness measurements of various films were carried out with profilometer and ellipsometer. The various spectra of rubrene were obtained in the form of films prepared by vacuum deposition method on the quartz plate with a size of 2.0×2.0cm^2.

RESULTS AND DISCUSSION

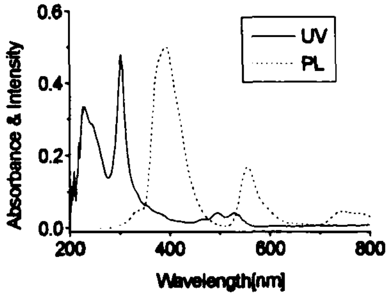

FIGURE 2. Photoluminescence and absorption spectra of rubrene film.

Figure 2 shows the photoluminescence spectrum and the absorption spectrum of rubrene in a form of the film. λmax were observed at 225nm, 300nm, 495nm, 526nm in the absorption spectra of rubrene. On the other hand, λmax of the photoluminescence spectra were observed at the wavelengh of 395nm and 551nm as shown in Figure 2. The measured optical band gap of rubrene was 2.16eV (570nm) and was in agreement with reported data[1] but was in disagreement with reported data (2.54eV, 2.40eV and 1.92eV)[2-4].

The Ag/Ag$^+$ electrode was calibrated at the beginning of the experiments by running cyclic voltammetry with ferrocene as the internal standard in an identical cell on the ITO working electrode. The potential values were referenced back to the saturated calomel electrode (SCE) potential by using the ferrocene/ferrocenium (Fc$^+$/Fc) couple as the internal standard. The potential values obtained versus Fc$^+$/Fc were converted to those versus SCE.

The reduction potential of ferrocenium versus normal hydrogen electrode (NHE) was 0.40V and reduction potential of SCE versus NHE was 0.24V. Therefore, the reduction potential of ferrocenium versus SCE was 0.16V. The reduction potential of ferrocenium versus Ag/Ag^+ was obtained as −0.20V in DMF. The potential values obtained versus Ag/Ag^+ were converted to those versus SCE by adding a constant of 0.36 in DMF to them. To transpose the measured redox behavior into the estimate for the ionization potential (IP) and electron affinity (EA), it is necessary to relate the electrochemical potentials to the vacuum level relative to which IP and EA are defined. An empirical relationship has been proposed by Brédas *et al.*[5] The expectation is as follows: $IP = E^{ox}(onset)+4.8$ and $EA = E^{Red}(onset)+4.8$.

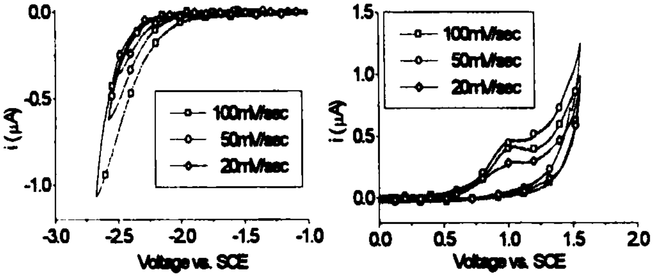

FIGURE 3. Cyclic voltammograms of rubrene.

Electrochemical measurements were performed using the cyclic voltammetry at room temperature and scan rate of 100~20 mV/sec in 0.1M Bu_4NClO_4 with DMF. The voltammograms measured for rubrene were shown in Figure 3. The oxidation onset potential and the reduction onset potential were measured to be +0.68V and −2.21V with the SCE electrode, which gave IP = 5.48eV, EA = 2.59eV and IP was almost agreement with reported data (5.51eV and 5.40eV)[4,6-8] but Eg = 2.89eV was in disagreement with reported data (2.54eV, 2.40eV, 2.2eV and 1.92eV) [1-4]. This indicates that there was a difference between the Eg and EA obtained from the optical gap and the cyclic voltammetry for rubrene estimated from the absorption band edge, which may be due to the different measuring methodology. Since the electroluminescent process is more close to the elcetrochemical process rather than the optical process, our values seems to be more reliable to explain the EL process.

CONCLUSION

We developed new cyclic voltammetry for organic materials for organic EL application. It was found that IP value of rubrene obtained using new cyclic voltammetry was in a good agreeement with the values published previously, but EA value was not.

ACKNOWLEDGEMENTS

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