

# Analysis of Deteriorated Species of ETL Generated with Metal Electrode Deposition by Liquid Extraction Surface Analysis Nanoelectrospray Ionization Mass Spectrometry

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Keywords: organic light emitting diode; damage due to electrode deposition; metal organic interface; Alq<sub>3</sub>; TPBi

## ABSTRACT

The chemical species formed on the ELT caused by the electrode deposition are analyzed by liquid extraction surface analysis (LESA) nano ESI-Orbitrap MS. N-oxygenated and N-hydrogenated molecules of 8-hydroxyquinoline and Alq<sub>3</sub> with a wide range of N values and generation of several decomposition components on TPBi are detected and characterized.

## 1 INTRODUCTION

During the manufacture of organic light-emitting diodes (OLEDs), the formation of an electrode on the organic film is essential. To satisfy the required optical and electronic properties, dry processes, such as vacuum evaporation and sputtering, are mainly used to manufacture electrodes on the organic films. However, high-temperature and/or chemically reactive particles used in a dry process are likely to cause decomposition of organic molecules [1]. Such damage at the interfaces between organic films and electrodes may result in formation of charged defects, modifying the barrier for charge injection, or of trap states in the organic material, reducing carrier mobility. Clarifying the nature of the interface between the organic materials and the electrode, including the decomposition products, is crucial for understanding and developing organic thin-film devices.

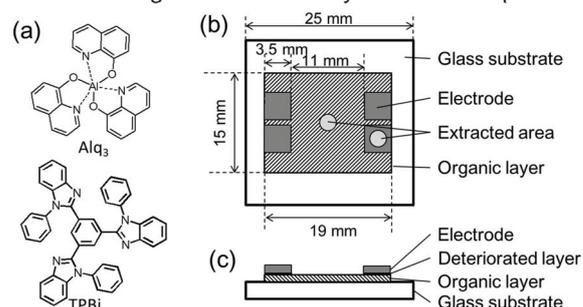
Liquid extraction surface analysis nanoelectrospray ionization mass spectrometry (LESA nano-ESI-MS) is a relatively new analysis method [2]. LESA nano-ESI has a two-step procedure involving (i) extracting analytes on the spatially resolved surface of interest via a liquid droplet held in suspension (liquid junction) and (ii) spraying the solvent through a nano-ESI silicon chip, which results in highly efficient ionization and a long-lasting, stable spray from several  $\mu\text{L}$  of sample. Compared to SIMS, which is usually used in surface mass analysis, ESI is an extremely soft ionization method, which rarely involves molecular fragmentation. We combined LESA nano-ESI with high-resolution MS analysis using an Orbitrap® mass spectrometer, which provides accurate masses and enables determination of the chemical formulae of molecular ions of extracted analytes from their exact masses. It is also highly advantageous that the high-resolution mass spectrum is less susceptible to

interference by contaminants, even in the case of an infusion mass spectrum. We have recently reported that LESA nano-ESI-MS can be used for the sensitive analysis of the hydrogenation and oxygenation components of 8-hydroxyquinoline formed on the surface of Tris(8-hydroxyquinoline) aluminum (Alq<sub>3</sub>) thin films by several cathode materials, Al, ITO, and MgAg [3]. In this report, in addition to our previous results, we report the results of the analysis of the oxygenation component of the Alq<sub>3</sub> complex and the successful detection and characterization of a wide range of decomposed chemical species of 2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi), which is attracted much attention as an electron transport material as well as Alq<sub>3</sub>, by using LESA nano-ESI-MS.

## 2 EXPERIMENT

### 2.1 Materials

Figure 1 shows the molecular structures of Alq<sub>3</sub> and TPBi and schematics of planar and cross-sectional views of the manufactured specimens. Hereafter, notation such as A/Alq<sub>3</sub> indicates a system prepared by depositing cathode A on Alq<sub>3</sub>. Al, ITO, and MgAg were used as cathode materials. An Alq<sub>3</sub> film with a length of 19 mm, a width of 15 mm, and a thickness of 10 nm was formed on a glass substrate by vacuum evaporation.



**Figure 1 (a) Molecular structure of Alq<sub>3</sub> and TPBi. Schematics of (b) the plain view and (c) the cross-sectional view of the specimen**

The detailed device structure and deposition conditions are described in the previous report[3]. The structure and deposition conditions of TPBi are also similar as in the Alq<sub>3</sub> device. The deposited samples were

immediately glass encapsulated in a nitrogen atmosphere, and the glass encapsulation was dismantled immediately before the LESA nano-ESI-MS measurements.

## 2.2 LESA Nano-ESI-MS Measurement

LESA nano-ESI-MS spectra were acquired using a TriVersa NanoMate robotic system (Advion, Ithaca, NY) coupled to an Orbitrap Q Exactive-Plus mass spectrometer (Thermo Scientific, Waltham, MA). A mixture of 2-propanol and acetonitrile (1:1 v/v containing 0.1vol% formic acid) was used as the extraction solvent. The extraction solvent (2  $\mu$ L) manipulated with a robotic pipette tip was dropped to form a microjunction with a diameter of about 2 mm between the solvent drop and the sample. After dismantling the glass encapsulation, Scotch tape was attached to the top of the cathode layer of the device under ambient conditions, and the tape was detached to peel off the cathode layer. LESA nano-ESI-MS measurements were executed at three points, i.e., on the surface without electrode (w/o electrode), the surface of the organic film side (organic side), and the surface of the electrode (electrode side). The measurements were performed in positive ionization mode with a scan range from  $m/z$  100 to 1,500 at a mass resolution of 140,000 and MS/MS scanning (FWHM at  $m/z$  200; high collision-induced dissociation, average 60 eV), and the accumulation time of the mass spectrum was 1 min. The observed peak intensity of each ion was normalized to the signal  $m/z$  146.0606 of the protonated 8-hydroxyquinoline molecule for Alq<sub>3</sub> and normalized to the signal  $m/z$  655.2595 of the protonated TPBi ion for TPBi experiment. Detailed experimental conditions for sample preparation and mass spectrometry have also been described in the previous report [3].

## 3 Results and Discussion

### 3.1 Study of oxygenation and hydrogenation of 8-hydroxyquinoline and Alq<sub>3</sub> generated by electrode deposition

Figure 2 shows the LESA nano-ESI mass spectrum (within the  $m/z$  100–500 range) of positive ions extracted with the solvent from the surface of the Al/ Alq<sub>3</sub> w/o electrode. The protonated molecular ion of Alq<sub>3</sub> complex is detected at  $m/z$  460.1231. The most intense peak at  $m/z$  146.0599 is assigned to the protonated 8-hydroxyquinoline, which is thought to be dissociated from the coordination complex of Alq<sub>3</sub> dissolved in the mixed solution of 2-propanol/acetonitrile. *N*-oxygenated and *N*-hydrogenated molecules of 8-hydroxyquinoline with a wide range of *N* values (*N* indicates the number of additional hydrogen or oxygen atoms) generated by the deposition of metal electrodes are detected by LESA nano-ESI-MS [1]. To visualize the formation behavior of the hydrogenated and oxygenated molecules created by the electrode deposition, the ion intensities of the oxygenated and hydrogenated molecules are displayed in

3D plots (hereinafter, such a 3D plot is called an “Ox–Hy plot”). Figure 3 shows the Ox–Hy plots of the w/o electrode and electrode side for each Alq<sub>3</sub> sample.

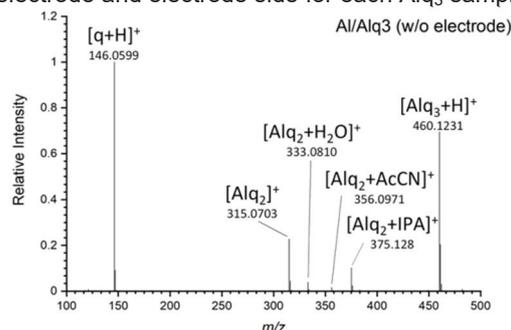


Figure 2 Positive ion LESA nano-ESI-MS spectrum obtained for Al/Alq<sub>3</sub>

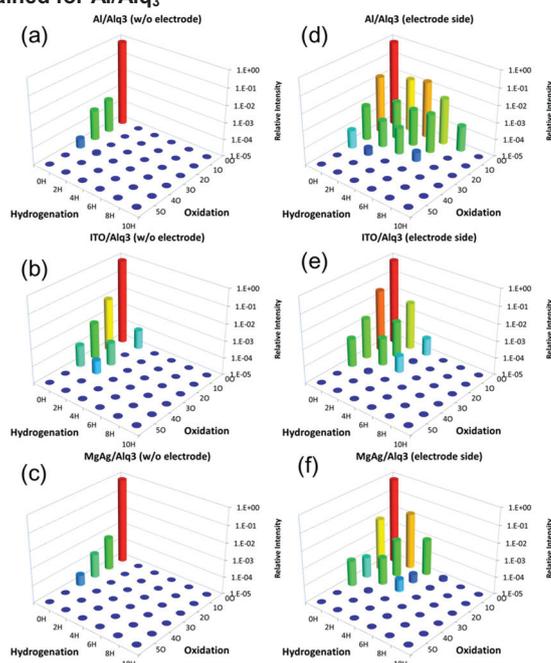
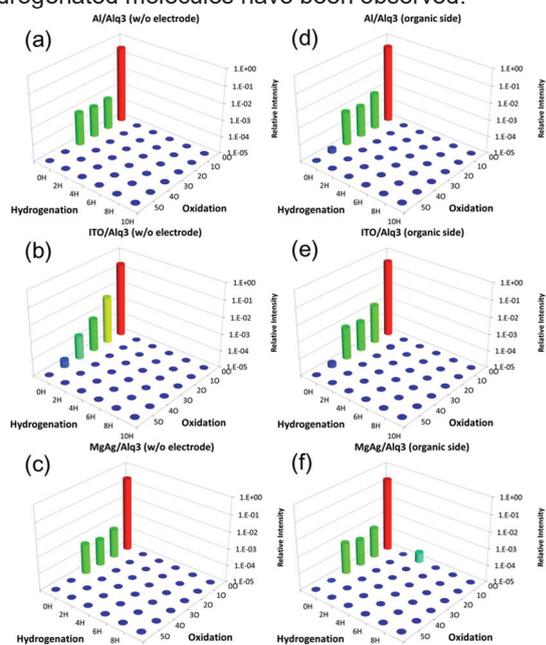


Figure 3 Ox–Hy plots of 8-hydroxyquinoline molecules of (a) Al, (b) ITO, (c) MgAg (w/o electrode), (d) Al, (e) ITO, and (f) MgAg (electrode side)

Hydrogenated molecules are hardly observed in the w/o electrodes of Al/Alq<sub>3</sub> and MgAg/Alq<sub>3</sub>. Figure 3b shows the Ox–Hy plot of the w/o electrode of ITO/Alq<sub>3</sub>. Here, the intensities of the oxygenated molecular ions are larger than those for the other two samples, and two hydrogenated molecules are observed in Figure 3b. According to Figure 3d, e, and f, oxygenation and hydrogenation of the 8-hydroxyquinoline occur simultaneously in all the electrode depositions. The molecular ions of two to twelve hydrogenated molecules with zero to three oxygenated species are observed in the electrode side of Al/Alq<sub>3</sub>. Since the relative ion intensities of one, two, and three oxygenated molecules decrease stepwise, oxidation of the 8-hydroxyquinoline molecules is thought to proceed stochastically. However, the two, four, and six hydrogenated molecules of unoxidized species have almost the same relative ion

intensities. Therefore, the four and six hydrogenated species might not be generated sequentially during the Al electrode deposition process; that is, the four and six hydrogenated species tend to be generated directly from the 8-hydroxyquinoline molecules when Al atoms are deposited on the Alq<sub>3</sub> surface. Figure 3e shows the Ox–Hy plot of the electrode side of ITO/Alq<sub>3</sub>. The distributions of the ion intensities of the oxygenated and hydrogenated species shown in Figure 3e are significantly different from those on the electrode side of Al/Alq<sub>3</sub> (Figure 3d). The ion intensity decreases drastically as oxygenation and hydrogenation of the molecules progress, so that oxygenation and hydrogenation of the 8-hydroxyquinoline molecules are thought to proceed sequentially.

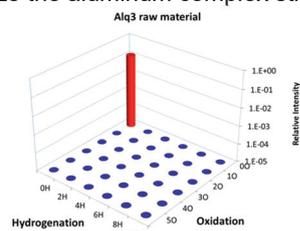
Figure 4 shows the Ox–Hy plots of the w/o electrode and electrode side of Alq<sub>3</sub> for each sample. Figure 4(d), (e), (f) show comparisons of organic side Ox–Hy plots of the protonated molecular ions of the Alq<sub>3</sub> complex. Plots of the w/o electrode are shown in (a) to (c). Oxygenated molecules of Alq<sub>3</sub> have been detected, but few hydrogenated molecules have been observed.



**Figure 4** Ox–Hy plots of Alq<sub>3</sub> molecules of (a)Al, (b)ITO, (c) MgAg for w/o electrode, (d) Al, (e) ITO, (f) MgAg for organic side

The relative intensities of the ions of molecules with one to three oxygens are almost identical for Al and MgAg deposition for w/o electrode samples. There are almost no changes in the intensity at w/o electrode and organic side sample. The Ox–Hy plots of the raw material of Alq<sub>3</sub> are shown in the Figure 5. Oxygenated nor hydrogenated molecules are undetectable, suggesting that in the case of Al and Mg deposition, the oxygenated molecule of Alq<sub>3</sub> complexes is presumed to be generated by heating during the deposition process. Given the same ion intensities of one to three oxygenated molecules, the oxygenation of

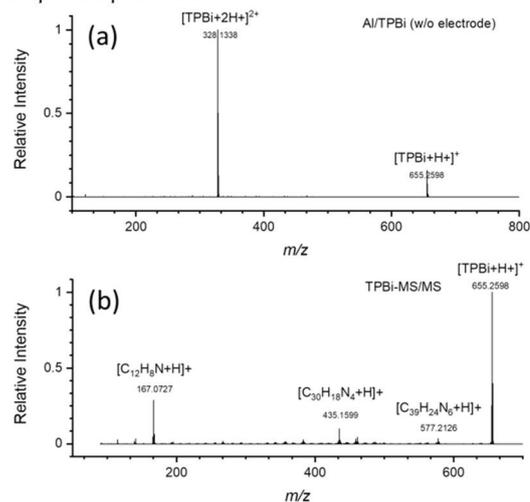
Alq<sub>3</sub> during heating is not seemed to be sequential reaction, but to be simultaneous reaction. In all cases, no hydrogen adducts are detected, which may be due to the fact that the 8-hydroxyquinoline structure is significantly destabilized in the case of hydrogenation, and the structure of the aluminum complex cannot be maintained in the solvent. On the other hand, in the case of oxygenation, the planarity of the 8-hydroxyquinoline is preserved, and the aluminum complex is stable rather than hydrogenation, indicating that the structure of the complex can be preserved in the solvent. Although up to three oxygenated molecule of 8-hydroxyquinoline have been detected, four oxygenated Alq<sub>3</sub> molecules are hardly detected, so that two or three oxygenated 8-hydroxyquinoline is considered to destroy the structure and destabilize the aluminum complex structure.



**Figure 5** Ox–Hy plots of Alq<sub>3</sub> molecules of raw material

### 3.2 Study on the similarity between the MS/MS fragmentation and decomposition formed by electrode deposition of TPBi

The structure of TPBi consists of a central benzene ring and three benzimidazole groups with a phenyl ring, which may be decomposed in these units by active particles during electrode deposition. In order to predict the structure of the decomposition products, we compare the fragment ions generated by the collision-induced dissociation (CID) system with the decomposed products.



**Figure 6** Positive ion LESA nano-ESI-MS spectrum obtained for (a) TPBi raw material and (b) MS/MS spectrum of TPBi.

Table 1 Comparison of Fragment ions of TPBi in MS/MS (CID) and detected ions in Electrode/TPBi

(a) MS/MS Measurement (CID) of TPBi

Experimental Mass	Relative Intensity	Estimated Molecular Formula	Theoretical Mass	Delta PPM	Neutral Loss
655.2597	100	[C45H30N6+H] <sup>+</sup>	655.2605	-1.2	
167.0727	28.15	[C12H8N+H] <sup>+</sup>	167.0730	-1.5	C33H22N5
168.0802	5.79	[C12H9N+H] <sup>+</sup>	168.0808	-3.4	C33H21N5
166.0649	4.34	[C12H7N+H] <sup>+</sup>	166.0651	-1.4	C33H23N5
435.1599	9.77	[C30H18N4+H] <sup>+</sup>	435.1604	-1.2	C15H12N2
433.1443	1.66	[C30H16N4+H] <sup>+</sup>	433.1448	-1.1	C15H14N2
577.2126	3.51	[C39H24N6+H] <sup>+</sup>	577.2135	-1.6	C6H6
141.0697	3.15	[C11H8+H] <sup>+</sup>	141.0699	-1.3	C34H22N6
139.0541	1.53	[C11H6+H] <sup>+</sup>	139.0542	-0.9	C34H24N6
459.1596	3.14	[C32H18N4+H] <sup>+</sup>	459.1604	-1.8	C13H12N2
458.1509	1.06	[C32H17N4+H] <sup>+</sup>	458.1526	-3.7	C13H13N2
383.1284	2.87	[C26H14N4+H] <sup>+</sup>	383.1291	-1.9	C19H16N2
382.1205	1.35	[C26H13N4+H] <sup>+</sup>	382.1213	-2.1	C19H17N2
267.092	1.39	[C19H10N2+H] <sup>+</sup>	267.0917	1.2	C26H20N4
195.0914	1.22	[C13H10N2+H] <sup>+</sup>	195.0917	-1.4	C32H20N4
356.118	1.16	[C25H13N3+H] <sup>+</sup>	356.1182	-0.6	C20H17N3

(b) Detected ions of LESA nano-ESI MS Experiment in Electrode(Al,ITO,MgAg)/TPBi Samples

Experimental Mass (Ave)	Detected Molecular ions	Theoretical Mass	Delta PPM	Assignment
655.2595	[C45H30N6+H] <sup>+</sup>	655.2605	-1.4	TPBi
170.0962	[C12H11N+H] <sup>+</sup>	170.0964	-1.4	DPA
488.1848	[C33H21N5+H] <sup>+</sup>	488.1870	-4.4	PBi-P(CN)-PBi
437.1746	[C30H20N4+H] <sup>+</sup>	437.1761	-3.5	PBi-(C=C)2-PBi
219.0904	[C15H10N2+H] <sup>+</sup>	219.0917	-5.8	PBi-CH=CH2
579.2312	[C39H26N6+H] <sup>+</sup>	579.2292	3.4	PBi-P(Bi)-PBi
463.1910	[C32H22N4+H] <sup>+</sup>	463.1917	-1.5	PBi-P-PBi
195.0914	[C13H10N2+H] <sup>+</sup>	195.0917	-1.3	PBi
387.1600	[C26H18N4+H] <sup>+</sup>	387.1604	-1.2	PBi-P-Bi
271.1216	[C19H14N2+H] <sup>+</sup>	271.1230	-4.9	P-PBi
387.1600	[C26H18N4+H] <sup>+</sup>	387.1604	-1.2	PBi-P-Bi
195.0914	[C13H10N2+H] <sup>+</sup>	195.0917	-1.3	PBi
463.1910	[C32H22N4+H] <sup>+</sup>	463.1917	-1.5	PBi-P-PBi
295.1094	[C20H12N3+H] <sup>+</sup>	295.1104	-3.4	PBi-P(CN)

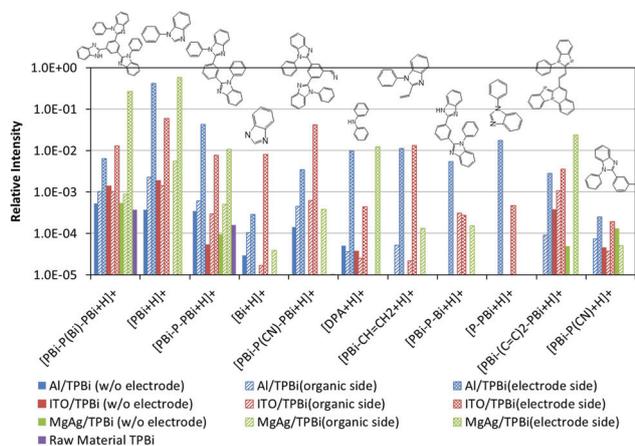


Figure 7 Relative ion intensities of decomposed species of the TPBi molecules obtained for the different locations.

MS/MS method, such as CID, has been popularized as a method to estimate and characterize the chemical structure of precursor ions from the mass number of fragment ions produced by dissociation in the gas phase. The high-resolution mass spectrum of TPBi and the MS/MS spectrum of protonated TPBi ion are shown in the Figure 6. Comparison of the fragment ions of the MS/MS spectrum of TPBi and the LESA experimental results of the thin TPBi film with metal electrode deposition is listed in the Table 1. Figure 7 shows the relative intensities of the molecular ions of the species generated by the electrode deposition to the hydrogenated TPBi ions for each sample. Although no clear trend is observed between the electrodes, the relative intensity of the ions derived from the degradation products of TPBi increased on the electrode side and the organic side sample. As shown in the Table 1, in addition to the molecules produced by the cleavage of the sigma bond between each aromatic unit of TPBi, the decomposed molecular ions estimated to be

divided between the two and four carbons of the central benzene ring are generated by the fragmentation and electrode deposition. The chemical species formed in the CID are quite similar to those formed on the surface of the organic film due to the collision of the reactive species during electrode deposition. The collision-induced fragmentation method of the mass spectrometer is found to be an effective method for predicting the degradation products of the organic materials due to electrode deposition.

#### 4 CONCLUSIONS

LESA nano-ESI-MS was successfully applied to detection of deteriorated species of typical electron transporting material, Alq<sub>3</sub> and TPBi, generated by the deposition of several metal electrodes; Al, ITO and MgAg. The relative ion intensities assigned to the N-oxygenated and N-hydrogenated 8-hydroxyquinoline molecules with a wide range of N values, generated by the electrode deposition, were compared in detail using 3D plots. Several decomposed species of TPBi are detected and compared with the fragment ions of MS/MS (collision induced dissociation) spectrum. Good agreement is found between the chemical species produced by the metal deposition and the fragment ions observed in the MS/MS spectra. The Nano-ESI-Orbitrap MS method is shown to be very effective for the characterization of degradable components of organic thin films by electrode deposition.

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