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Abstract

Interfaces in polymer light emitting diodes (PLED) made from poly(1,4 phenylene vinylene) (PPV) on indium tin oxide (ITO) substrate with evaporated Mg as a negative electrode, have been studied by X-ray photoelectron spectroscopy (XPS). Thin films of PPV on ITO were prepared by thermal conversion of undialyzed and dialyzed sulfonium precursor polymer, and Mg was evaporated on top under high vacuum conditions. Characterization of PPV by XPS indicated that two different polymer surfaces are obtained by using undialyzed and dialyzed precursor polymer. Without dialysis, more oxygen impurities are present on the polymer surface, and this has been shown to lead to differences in observations associated with subsequent processing steps. For example, upon metal deposition under high vacuum conditions the polymer surface appears more reactive to oxygen and the formation of Mg carbide is noticed. Much purer PPV can be synthesized from the dialyzed precursor, but still oxidation of the polymer/metal interface occurs when the Mg source is used under high vacuum conditions, although no evidence was found for Mg carbide formation. The relative amounts of the different carbon components detected by XPS after metal evaporation on the polymer/metal interface have been shown to depend strongly on the details of the PPV preparation process (especially on whether undialyzed or dialyzed precursor is used).

A new two-layer polymer diode, using an ion exchange resin Nafion® with incorporated tris (2,2′-bipyridine) ruthenium (II) complex \{Ru(bpy)_3^{2+}\} placed between PPV and the metal electrode, was fabricated and its electroluminescence properties tested. Interfaces in such a diode were studied by XPS. Studies of the interaction between Nafion and the Ru\(^{2+}\) complex indicated that a substantial surface rearranging occurs upon exposing the Nafion to the aqueous solution of Ru\(^{2+}\) complex. The hydrophilic sulfonic groups, which exist in a form of clusters among the
hydrophobic fluorocarbon chains in the Nafion, become more oriented to the surface due to the hydrophilic interaction. A further driving force for this rearrangement is believed to originate from the electrostatic interactions between the Ru$^{2+}$ complex and SO$_3^-$ groups on Nafion, as well as SO$_4^{2-}$ ions formed by oxidation. XPS indicates that the amount of S-groups oriented toward the Nafion surface is a function of the thickness of the Nafion + Ru$^{2+}$ complex film, and in particular the thinner the film the greater the structural rearrangement. XPS characterization of an interface formed between thin film of Nafion + Ru(bpy)$_3^{2+}$ on PPV and Mg evaporated under high vacuum, indicated that the Mg interacts directly with the fluorocarbon part of the Nafion polymer, although oxygen is also picked up at this interface for the conditions used.

Electroluminescence testing of the fabricated Mg/Nafion + Ru(bpy)$_3^{2+}$/PPV/ITO diode showed yellowish light emission in spark form for values of applied current in the range 23-57 mA, while red light was emitted for 10 sec at the higher current of 63 mA. The I-V characteristic curve measured for this device followed expectations for diode behavior.
# Table of Contents

Abstract ii

Table of Contents iv

List of Tables vi

List of Figures vii

Acknowledgments x

Chapter 1 Polymer Light Emitting Diodes 1

1.1 Introduction 1

1.2 Mechanism of Light Emission 5

1.3 Two-Layer Devices 7

1.4 Other Attempts at PLED Design 9

1.5 Characterization of PLEDs 10

1.6 New Possibilities for PLEDs Design 12

1.7 Aims of Research 14

Chapter 2 X-Ray Photoelectron Spectroscopy 15

2.1 Introduction and Basic Principles 15

2.1.1 Spectral Features 18

2.1.2 Quantitative Analysis 21

2.2 Instrumentation 22

2.2.1 Ultrahigh vacuum System 22

2.2.2 Sample Handling 24

2.2.3 X-Ray Source 26

2.2.4 Energy Analyzer 27
2.2.5 Data Processing

Chapter 3 Experimental

3.1 Sample Preparation
3.2 High Vacuum System for PLED Preparation
3.3 Sample Characterization

Chapter 4 Studies of Interfaces in Mg/PPV/ITO Diode

4.1 XPS Studies of Undialyzed PPV Film on ITO Substrate
4.2 XPS Studies of Mg/undialyzed PPV Interface
4.3 XPS Studies of Dialyzed PPV and Its Interface With Mg

Chapter 5 Studies of Interfaces in Mg/Nafion + Ru(bpy)$_3^{2+}$/PPV/ITO Diode

5.1 Introduction
5.2 XPS Studies of Nafion
5.3 XPS Studies of Nafion With Ion Exchanged Ru(bpy)$_3^{2+}$
5.4 XPS Characterization of a Nafion + Ru(bpy)$_3^{2+}$ Film Deposited on PPV
5.5 Mg Deposition on the Nafion + Ru(bpy)$_3^{2+}$/PPV/ITO Sample
5.6 Electroluminescence Testing of the Mg/Nafion + Ru(bpy)$_3^{2+}$/PPV/ITO Diode

Chapter 6 Concluding Remarks and Future Work

6.1 Summary of Results
6.2 Future work

References
### List of Tables

<table>
<thead>
<tr>
<th>Table 4.1</th>
<th>Relative atomic compositions for PPV film deduced from spectrum in Fig. 4.1.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 4.2</td>
<td>Relative atomic compositions for Mg/PPV sample deduced from spectrum in Fig. 4.4.</td>
</tr>
<tr>
<td>Table 4.3</td>
<td>Relative amounts according to XPS of different carbon components before and after Mg deposition on PPV.</td>
</tr>
<tr>
<td>Table 4.4</td>
<td>Relative atomic compositions for Mg/dialyzed PPV sample deduced from spectrum in Fig. 4.9.</td>
</tr>
<tr>
<td>Table 4.5</td>
<td>Relative amounts for different carbon components identified in C 1s spectra measured from dialyzed PPV before and after Mg deposition.</td>
</tr>
<tr>
<td>Table 5.2</td>
<td>Relative atomic composition of Nafion from chemical formula and from XPS.</td>
</tr>
<tr>
<td>Table 5.2</td>
<td>Relative intensities of different carbon components in samples before and after Mg deposition on the Nafion + Ru(bpy)$_3^{2+}$/PPV sample.</td>
</tr>
</tbody>
</table>
List of Figures

Figure 1.1 Schematic indication of (a) polymer light emitting diode; (b) energy diagram for valence and conduction bands in insulator, semiconductor and metallic materials ($E_g$ identifies the band gap for the first two).

Figure 1.2 Chemical structure of some light emitting polymers.

Figure 1.3 Schematic indications of (a) structure of some polarons and bipolaron formed in PPP; (b) radiative decay of singlet exciton.

Figure 1.4 Band scheme of a two-layer device under forward bias. Positions of the Fermi energies for the electrode materials with respect to HOMO and LUMO levels are illustrated.

Figure 1.5 I-V characteristic compared with light intensity measured for a ITO/PPV/Ca diode [72].

Figure 1.6 Chemical formula of Nafion® perfluorinated polymer.

Figure 2.1 Schematic diagram for (a) photoelectric effect; (b) x-ray fluorescence and (c) Auger emission.

Figure 2.2 (a) A low resolution XPS spectrum for ITO sample and (b) a high resolution In 3d spectrum excited by Al Kα.

Figure 2.3 Intensity contribution from an infinitesimal thickness dx in a semi-finite sample.

Figure 2.4 A schematic diagram of the MAX200 system viewed from top.

Figure 2.5 Schematic representation of the pumping system for the MAX200.

Figure 2.6 Dual anode X-ray source.

Figure 2.7 Schematic representation of the pumping system for the MAX200.

Figure 2.8 Schematic diagram of the relevant energy levels for the binding energy measured by spectrometer.

Figure 2.9 Shirley non-linear background subtraction applied to a Mg 2p narrow scan spectrum.

Figure 2.10 Narrow scan spectrum for C 1s signal in Nafion sample: (a) unfitted and (b) after fitting of different components.

Figure 3.1 Schematic representation of PPV synthesis.
Figure 3.2  Diode fabrication: (a) etched ITO substrate and (b) after polymer and metal deposition.

Figure 3.3  Design of high vacuum system for PLED preparation.

Figure 3.4  Design of evaporation source.

Figure 4.1  XPS survey spectrum from PPV on ITO sample.

Figure 4.2  C 1s spectrum for PPV.

Figure 4.3  (a) Fitted C 1s spectrum and (b) O 1s spectrum in PPV.

Figure 4.4  XPS survey spectrum from PPV with evaporated Mg.

Figure 4.5  C 1s spectrum from PPV after Mg deposition: (a) raw spectrum and (b) after curve fitting process.

Figure 4.6  XPS spectra for PPV after Mg deposition: (a) O 1s and (b) Mg 2p.

Figure 4.7  XPS survey spectrum measured from dialyzed PPV sample.

Figure 4.8  High resolution spectra for dialyzed PPV: (a) C 1s and (b) O 1s.

Figure 4.9  XPS survey spectrum measured from dialyzed PPV after Mg deposition.

Figure 4.10  C 1s spectrum for Mg/dialyzed PPV sample.

Figure 4.11  High resolution spectra for Mg/dialyzed PPV: (a) O 1s and (b) Mg 2p.

Figure 5.1  (a) Chemical formula of Nafion®, and (b) schematic indication of the three phase model.

Figure 5.2  Low resolution XPS spectrum measured for Nafion.

Figure 5.3  High resolution spectra measured for Nafion: (a) C 1s and (b) O 1s.

Figure 5.4  High resolution spectra measured for Nafion: (a) F 1s and (b) S 2p.

Figure 5.5  Low resolution XPS spectrum measured for Nafion + Ru²⁺ complex sample.

Figure 5.6  C 1s spectrum measured for Nafion + Ru²⁺ complex sample.
Figure 5.7 Comparison of S 2p spectra for Nafion and Nafion + Ru\(^{2+}\) complex samples: (a) unfitted spectrum from Nafion; (b) unfitted spectrum from Nafion + Ru\(^{2+}\) complex; (c) fitted spectrum to show components in (a); and (d) fitted spectrum to show components in spectrum (b).

Figure 5.8 Comparison of O 1s spectra measured from: (a) Nafion and (b) Nafion + Ru\(^{2+}\) complex sample.

Figure 5.9 Comparison of C 1s spectra: (a) sample A (thick Nafion + Ru\(^{2+}\) complex film); (b) sample B (thin Nafion + Ru\(^{2+}\) complex film on PPV); and (c) fitted spectrum (a) to show components.

Figure 5.10 High resolution spectra measured from sample B (thin Nafion + Ru\(^{2+}\) complex film) on PPV: (a) O 1s and (b) S 2p.

Figure 5.11 Comparison of C 1s spectra measured from: (a) Nafion + Ru\(^{2+}\) complex thin film on PPV; (b) sample in (a) after deposition of Mg thin film; and (c) sample in (a) after deposition of more Mg (i.e. to form thicker film).

Figure 5.12 High resolution spectra measured from Nafion + Ru\(^{2+}\) complex thin film on PPV: (a) C 1s and (b) O 1s.

Figure 5.13 Comparison of F 1s spectra measured from Nafion + Ru\(^{2+}\) complex on PPV after Mg deposition: (a) thin Mg layer and (b) thicker Mg layer.

Figure 5.14 Mg 2p spectra measured from Nafion + Ru\(^{2+}\) complex/PPV sample after Mg deposition: (a) thin Mg film and (b) thicker Mg film.

Figure 5.15 Plasmon excitations measured in low resolution spectra from Mg/Nafion + Ru\(^{2+}\) complex/PPV samples: (a) thin Mg film and (b) thicker Mg film.

Figure 5.16 I-V characteristic curve measured for a Mg/Nafion+Ru(bpy)$_3^{2+}$/PPV/ITO diode.
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Chapter 1  Polymer Light Emitting Diodes

1.1  Introduction

The traditional role of plastic materials acting just as insulators was changed by the discovery in the mid 1970s of a new generation of polymeric materials with good electrical conductivity [1]. These new materials have favorable physical and mechanical properties (light weight, physical strength, ease of processibility), which combined with the electronic functionality of metals and semiconductors, have offered a remarkable opportunity for a wide range of applications in the electronic industry.

The majority of the new plastic conductors, synthesized in the last 20 years, are conjugated polymers which have planar or nearly planar sequences of alternating single and double bonds along the polymer backbone chain. Doped conjugated polymers have achieved conductivities up to $10^3 - 10^5 \, \Omega^{-1}\, \text{cm}^{-1}$ which enables their use for conductive coatings [2]. For comparison, conductivities of Cu, Al, Au are in the $10^6 - 10^8 \, \Omega^{-1}\, \text{cm}^{-1}$ range while doped Si is ~ $10^2 \, \Omega^{-1}\, \text{cm}^{-1}$ [3,4].

Interest in applications of conjugated polymers in thin film semiconductor devices started in the late 1980s, after the first polymer field effect transistor was made [5,6]. The subsequent discovery of electroluminescence from conjugated polymers (i.e. emission of light when excited by flow of electric current) in 1990 [7], has led to much interest in the development of novel polymer light emitting diodes (PLEDs) for organic display technology purposes [8]. This chapter gives a brief overview of progress made in this area.

The basic structure of a PLED is illustrated in Fig. 1.1 (a). A film of polymer (thickness about 100 nm) is sandwiched between two electrodes. The positive electrode is commonly a
Figure 1.1  Schematic indications of (a) polymer light emitting diode; (b) energy diagram for valence and conduction bands in insulator, semiconductor and metallic materials ($E_g$ identifies the band gap for the first two).
transparent thin film of indium-tin oxide (ITO) deposited on glass substrate, while the negative electrode is a low work function metal (e.g. Al, Ca or Mg). The diode emits light through the transparent substrate when the electrodes are connected to a battery.

Conjugated polymers belong to the class of semiconductor materials which have a filled valence band an empty conduction band and a relatively small energy gap between them. Figure 1.1 (b) schematically represents the bands of energy levels in an insulator (large band gap), a semiconductor (small band gap) and a metallic conductor with an unfilled valence band according to the band theory.

In the past forty years, inorganic semiconducting materials such as GaAs, GaAsP and AlGaAs have been dominant in LED fabrication [9]. Epitaxial growth techniques have been used for their production as thin semiconductive layers. This process is expensive and is not suitable for production of large area displays. Conjugated polymers offer a number of advantages compared to other materials used for LED preparation [10] including:

1) large area of polymer thin films can be fabricated by a low-cost spin-coating process (i.e. by dropping the polymer solution onto a rotating substrate);

2) these devices can operate at low voltages (e.g. 5-10 V);

3) flexible substrates can be used [11,12];

4) the emission color can be tuned by modifying the band gap in the polymer (e.g. by changing the conjugation length, adding different side-attached groups);

Figure 1.2 illustrates the chemical structures of some conjugated polymers which exhibit electroluminescence. Poly(1,4 phenylene vinylene) (PPV) was the first polymer used to prepare a PLED and it is still a favorite one. Its band gap is 2.5 eV and this results in the emitting in yellow-green part of the spectrum [13,14]. Diodes made from its soluble derivatives, namely poly[2-methoxy-5-(2’-ethyl-hexoxy)-1,4-phenylene vinylene] (MEH-PPV) and cyano substituted
Figure 1.2 Chemical structure of some light emitting polymers.

PPV

PPP

MEH-PPV

Poly (3-alkylthiophene)

R: C_{12}H_{25}, C_{18}H_{37}, C_{10}H_{20}

CN-PPV
PPV (CN-PPV), emit red-orange light [15,16]. Derivatives of poly(3-alkylthiophene) can produce different colors depending on the nature of the side chains and the concentration of regioisomeric forms of polymer: head to head, head to tail...[17-20]. To obtain blue light, emitters with band gaps of about 3 eV are required, and this necessarily leads to an increased turn-on voltage (i.e. the applied voltage at which the light emission starts). “True blue” has been achieved by poly(p-phenylene) (PPP) conjugated polymer and its derivatives [21], and by attaching chromophores as side groups to partially conjugated polymers [22-24].

1.2 Mechanism of Light Emission

Light generation requires the diode to be biased sufficiently to achieve injection of positive and negative charge carriers from opposite electrodes. Electrons (from the metal cathode) are injected into the LUMO (i.e. the lowest unoccupied molecular orbital of the conduction band) of the polymer, and holes from the ITO anode pass to the HOMO (i.e. the highest occupied molecular orbital of the valence band). These injections create charge sites in the polymer chain, which as a result of electron-phonon interactions, give local structural distortions in the alternating bond configuration. These distorted excitation sites are called “polarons” and “bipolarons” [2,59,71] and an illustration is indicated in Fig. 1.3 (a) for the PPP polymer. Negative and positive polarons migrate under the influence of an applied electric field, and they can combine in a segment of polymer to form a singlet exciton (i.e. loosely bound electron-hole pair) which can decay radiatively as indicated in Fig. 1.3 (b). The decay of less mobile bipolarons is non-radiative [25]. The efficiency of light emission, which is expressed as the number of photons generated for each electron injected, strongly depends on the competition between these two processes, as well as on the number of holes injected and on the presence of defect sites which quench electroluminescence.
Figure 1.3  Schematic indications of (a) structure of some polarons and bipolaron formed in PPP; (b) radiative decay of singlet exciton.
Normally the injection of charge from an electrode requires overcoming a barrier formed at the polymer/electrode interface by the energy difference between the electrode Fermi level and the HOMO and LUMO levels for the polymer. The magnitude of the barrier can be estimated by measuring the dependence of current density vs. applied electric field across different PLEDs, as proposed by Parker [26]. For most light emitting polymers, ITO (work function, $\Phi_w = 4.8$ eV) provides a good match for hole injection since the barrier height is small, typically $0.2$ eV [27]. An even lower barrier value can be obtained by using polyaniline as a transparent hole injector electrode [28]. Since the match is more difficult for electron injection, low work function metals (e.g. Al, Mg, Ca) must be used to keep the barrier as low as possible. That constant imbalance between numbers of electrons and holes injected affects the effectiveness of the radiative recombinations. The mechanism of charge injection into the polymer and subsequent charge transport are still subject to intensive research. For charge injection, more than one possible mechanism exists, depending on the size of the barrier, the mobility of the carriers, the value of the applied electric field and the temperature [29,30,70]. Proposed mechanism for carrier transport includes thermal activation and variable range of hopping [69]. In PPV polymer holes are more mobile than electrons, and this fits the typical case for polymers with relatively low ionization energy and low electron affinity [31].

1.3 Two-Layer Devices

PLEDs fabricated using a combination of PPV and CN-PPV polymer layers, proved to have a lower turn-on voltage, and a higher efficiency and brightness compare with one of these layers alone [32]. It seems that the presence of the electron withdrawing cyano group, at the polymer-metal contact, improved the electron injection. On the other side, holes injected from ITO through the PPV layer were confined at the interface of the two polymers, because CN-PPV
has a poor hole conductivity. Thus, the radiative recombination occurred away from the polymer/electrode interfaces, which are normally sources of quenching sites. An energy level diagram for a two-layer device is illustrated in Fig. 1.4.

![Energy level diagram for a two-layer device](image)

Figure 1.4 Band scheme for a two-layer device under forward bias. Positions of the Fermi energies for the electrode metals with respect to HOMO and LUMO levels are illustrated.

A better balance between the number of carriers injected, compared to the situation for one-layer devices, has also been achieved by introducing an additional layer of 2-(4-bisphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) dispersed in poly(methyl methacrylate) (PMMA) [33]. Its good electron transport properties have also been used for the preparation of molecular organic LEDs [34]. Other polymers, with electron-deficient oxadiazole rings, placed between the emitting polymer and the metal electrode had the same effect [35].
1.4 Other Attempts at PLED Design

A variety of ideas have been applied in designing PLEDs for reaching the performance goals: greater stability, brightness, efficiency and life-time. Appropriate polymers have been dispersed in an insulating matrix, such as PMMA, to give a still-unexplained increase in diode efficiency, as well as showing the possibility for white light emission [36]. Semiconductive inorganic materials such as CdS have been combined with PPV to form a two-layer device [37]. Additionally, conjugated polymers have been blended with other similar materials [38,39], as well as with partially or non-conjugated materials and with organic dyes [40]. Blending may both improve the overall behavior and allow the possibility of color tuning. A blend of different poly(alkylthiophene) derivatives was used to construct a device in which the emission was tuned from red to green by controlling the applied voltage [41]. Color tuning has been achieved using copolymers as well [42]. They also affect the diode performance in terms of stability. Recently, a device made from PPV copolymer containing PPV segments and non-conjugated α-acetyloxy-p-xylylene units, proved to be stable for 12,000 h under continuous operation in air at room temperature [43].

At present, the main problems in PLED performances are: the photodegradation of polymers during operation, corrosion at the cathode, and the degradation of polymer/electrode interfaces. Studies on PPV have shown that photooxidation produces carbonyl defects in polymer chains that reduce conjugation and quench fluorescence [44]. The formation of singlet oxygen, upon light exposure in the presence of oxygen and moisture from air, leads to the degradation of MEH-PPV [45]. The presence of defect sites at the polymer surface, and at metal/oxide/polymer interfaces formed during metal deposition, also affects the electroluminescence. To prevent cathode corrosion (especially when Ca is used), the encapsulation of the diode with epoxy resin is necessary.
In just a few years, conjugated polymer LEDs are approaching a performance level which is comparable with inorganic diodes. Currently, the most successful PLEDs operate at below 5 V, with brightness in the range of one to several hundred Cd/m². Life-times can be in the 1000-12,000 h range for continuous operation under normal atmospheric condition, and this can be increased further by using a noble gas atmosphere. Storage and operating life-times of at least 5 years and 20,000 h respectively are needed for commercial applications (backlights for instrumentation panels, flat panel displays, TV screens...) [46].

At the beginning of 1998, the cooperation between the companies Cambridge Display Technology and Seiko-Epson yielded the world’s first video display based on a light emitting polymer, and it is clear that in this area technological developments are following very rapidly on scientific advances [47,48].

1.5 Characterization of PLEDs

The performances of PLEDs can be tested by measuring the current-voltage characteristic curves which provide information about rectification properties and turn-on voltages (Fig. 1.5). Changes in current density or intensity of luminescence during operation indicate the beginning of degradation, although these measurements do not provide information about what lead to the device failure.

The lifetime of a PLED depends on the detailed chemical and physical interactions, and insight into changes in chemical and electronic structures, for the conjugated polymers and their interactions with electrodes, can be obtained with surface science techniques.

The first example of studies of neutral and electrochemically doped states of poly(p-phenylene vinylene) (PPV), by a combination of X-ray photoelectron spectroscopy (XPS) and theoretical calculations, suggested the presence of condensed polymeric phase and nonuniformity
in distribution of positive charge over the polymeric matrix [49,50]. Sensitivity of PPV to air exposure has been established by measuring the O 1s signal in XPS for samples both exposed to air and heated in vacuum [51].

Figure 1.5 I-V characteristic compared with light intensity measured for a ITO /PPV /Ca diode [72].

Processes at the interfaces appear crucial for the overall performance of the diodes. To date, not much work has been done on the interfaces between conjugated polymers and the ITO transparent electrode. The influence of different cleaning procedures for ITO samples, and the interaction of these samples with polyaniline has been reported [52]. A combined experimental
function metals Ca, Al, Na, Rb and Mg. It was reported that the presence of surface oxygen defects results in metal-oxide formation in the case of Ca, and this changes the metal-induced surface band-bending at the polymer/metal interface [53,54]. The vapor deposition of Ca, Rb, Na and K on the conjugated polymer surface is generally accompanied by diffusion of metal atoms into the near surface region with n-type doping of the polymer [55,56,59]. Aluminum deposition results in covalent bond formation with oxygen defects on the surface; additionally interaction with the vinylene double bonds causes a breaking of conjugation in the polymer π system [59]. Schottky barrier formation and associated band bending at the PPV/Al interface has been investigated, but there is a debate on whether the chemical shift of the metallic Al 2p peak observed by XPS originates from band-bending or from growth of metal clusters [60-62].

Surface science techniques including XPS, scanning electron microscopy (SEM) and atomic force microscopy (AFM), have been used to investigate failure mechanisms in PLEDs [63-65]. Irregularities in the spin-coated polymer films, morphological changes during operation, as well as oxidation of both metal and polymer films have been indicated as factors in the degradation.

1.6 New Possibilities for PLEDs Design

We have explored the new possibility for designing PLEDs by using a layer of Nafion polymer with incorporated tris (2,2' - bipyridine) ruthenium (II) complex ion, {Ru(bpy)₃}²⁺, placed between PPV and a Mg electrode. We were hoping that the Mg/Nafion + Ru(bpy)₃²⁺/PPV/ITO device will exhibit electroluminescence, and that the Nafion + Ru²⁺ complex layer can possibly influence better electron injection. The first electroluminescent device based on the Ru(phen')₃²⁺ complex was recently shown to emit red-orange color [66]. To
our knowledge, no previous attempt at using Nafion as a matrix for ruthenium complexes in PLED design has been made.

Nafion is a perfluorinated polymer that consists of a backbone of tetrafluoroethylene with pendant side chains of perfluorinated vinyl ethers which terminate in sulfonic acid groups. Because of its thermal and chemical resistance, ion exchange properties, selectivity, mechanical strength and insolubility in water, Nafion has a wide range of commercial applications. Some typical uses are in liquid-gas separations, solid polymer fuel cells, dialysis and ion exchange, membrane-separated chlor-alkali cells, batteries, electrochemical processes, modified electrodes [67,68].

The chemical formula of Nafion is illustrated in Fig. 1.6. Various polymers with different molecular weights exist depending on the number of repeating units contained in the fluorocarbon chains (as defined by the numbers k,l,m). Nafion ® used in this work has k = 6.5, l = 1, m = 1 and this corresponds to the formula C$_{20}$ F$_{39}$ O$_5$ S H which is molecular weight of 1094 g/mol (sample from Aldrich is quoted at 1100 g/mol).

Figure 1.6 Chemical formula of Nafion ® perfluorinated polymer.
1.7 Aims of Research

The work in this thesis is focused on study of interfaces formed in two different types of polymer light emitting diodes. These are specified as follows:

1) a single-layer PPV device designated as Mg/PPV/ITO with thermally evaporated Mg as the metal electrode;

2) a new two-layer device designated as Mg/Nafion + Ru(bpy)$_3^{2+}$/PPV/ITO, and this has a layer of PPV and a layer of Nafion ion exchange resin with incorporated tris (2,2'- bipyridine) ruthenium (II) complex ion placed in between the PPV and the Mg electrode;

The objectives are to get more chemical information about the interfacial interactions occurring between the polymers and the electrodes for diodes prepared under high vacuum (HV) conditions, as well as to study interactions between Nafion and the ionically incorporated Ru$^{2+}$ complex, and to study interfacial changes as new layers are added in the device structure.

The thesis is organized as follows: Chapter 2 introduces basic principles for the XPS technique, while Chapter 3 describes the procedures used for preparing the polymer diodes under high vacuum conditions. Chapters 4 and 5 report XPS studies for the interfaces present in the two types of diode prepared as well as the initial device performance tests made in this work. Finally, Chapter 6 gives some conclusions and indicates directions for future work.
Chapter 2  X-Ray Photoelectron Spectroscopy

2.1  Introduction and Basic Principles

X-ray photoelectron spectroscopy (XPS) belongs to the category of analytical methods referred to as electron spectroscopy for chemical analysis. Electron energies are measured in XPS. It is a key technique for surface analysis and characterization of any solid material which is stable under vacuum conditions. Elemental analysis and chemical bonding information are provided (except for hydrogen and helium) for the topmost 50 Å or so from the surface [73,74].

The technique was developed after the discovery and explanation of the photoelectric effect. Hertz in the 1880s noticed that metal contacts in electrical systems show an enhanced ability to spark when exposed to light [75]. J.J. Thompson found that electrons are emitted from zinc plate after exposure to light [76]. The explanation for these experiments came from Einstein in 1905: *photons of light directly transfer their energy to electrons in the solid resulting in the emission of electrons with conservation of energy* [77].

The first experiments which used this phenomenon to perform an analytical function were done by Robinson and Rowlinson in 1914 [78]. Throughout the 1950s and 1960s, Siegbahn and coworkers [79] refined the instrumentation and approach, and shortly after the first commercial systems were developed.

The basic XPS experiment is illustrated in Fig. 2.1(a). The solid surface to be analyzed is first placed in a vacuum environment and then irradiated with photons in the soft X-ray range (typically ~ 1.5 keV). The atoms comprising the surface region emit electrons as a result of the direct transfer of photon energy to the solid, and this is especially to electrons in core orbitals. These photoelectrons are subsequently counted as a function of their kinetic energy.
This process can be described by the Einstein equation

\[ E_b = h\nu - E_k \]  \hspace{1cm} (2.1)

where \( E_b \) is the binding energy for the electron in the atom, \( h\nu \) is the energy of the X-ray photons and \( E_k \) is the measured kinetic energy of the emitted electrons. [73,74,80]. The binding energy measures the amount of energy required to remove a particular electron from the solid, and it provides information about the orbital energy, the nature of the atom and its chemical environment.

Once a photoelectron has been emitted, the resulting ion is in an excited state. The excess energy can then be dissipated through one of two relaxation processes: (1) emission of X-ray fluorescence; or (2) ejection of secondary (Auger) electrons, illustrated on Fig. 2.1 (b,c).

An XPS spectrum generally shows signals from Auger electron emission as well as photoemission. The kinetic energy of the emitted Auger electrons depends on the three energy levels involved, and for the example in Fig. 2.1(c) this is, to a first approximation:

\[ E_{KL1L23} = E_K - E_{L1} - E_{L23} \]  \hspace{1cm} (2.2)

where \( E_{KL1L23} \) is the kinetic energy of Auger electron, \( E_K \) is the binding energy of the initial core hole (K shell vacancy), while \( E_{L1} \) and \( E_{L23} \) are binding energies for the two orbitals in higher energy states [73].

Auger electrons can be distinguished from photoelectrons by their kinetic energy being independent of the energy of the incident radiation. Each element provides its characteristic set of Auger electron kinetic energies, and measurements of these spectra can also be very useful for analytical purposes.
Figure 2.1  Schematic diagram for (a) photoelectric effect; (b) x-ray fluorescence and (c) Auger emission.
2.1.1 Spectral Features

An XPS spectrum is displayed as a plot of ‘intensity’ or ‘number of counts’ (on the y-axis) against either kinetic energy or, more usually, binding energy on the x-axis. A measurement is typically performed by first taking a wide scan (or survey scan) spectrum covering a range of 1000 eV or so, and then looking in more detail at higher energy resolution over narrow energy ranges (e.g. 10-20 eV), to study specific features seen in the wide-scan spectrum [80]. Figure 2.2 (a) shows a survey scan of indium tin oxide (ITO) irradiated by an Al Kα source. Peaks seen are associated with core-level photoemission events and X-ray induced Auger electron emission. They can be identified by comparing their positions on the binding energy scale with tabulated data [82]. For example, the photoelectron peaks identified in Fig. 2.2 are expected to occur close to the following binding energy values: In 3s (824.2 eV), Sn 3d (706.4 eV), In 3p (666.6 eV), O 1s (533.0 eV), Sn 3d (487.1 eV), In 3d (443.2 eV), C 1s (285.0 eV), In 4s (122.0 eV), In 4p (78.2 eV) and In 4d (16.3 eV). The Auger electron peaks marked have binding energy values: C KLL (1226.6 eV), In MNN (1088.4 eV) and O KVV (976.6 eV).

Electrons with kinetic energies inside the solid in this energy range (e.g. < 1.5 keV) have a high probability of undergoing inelastic scattering with a consequent energy loss. This will happen when their path in the solid is relatively long, in which case they do not contribute to a sharp peak in the photoemission spectrum but rather to the spectral background (they then appear at an increased binding energy).

The low binding energy part of a spectrum (e.g. < 30 eV) corresponds to signals coming from the valence levels. This region is often less informative in XPS because of reduced probabilities for photoemission. The interaction between incident photons and valence electrons is increased when their energies are comparable. Therefore more information for valence
electrons can be obtained by using ultraviolet radiation, as in UV photoelectron spectroscopy (UPS) [81].

An XPS spectrum at high resolution provides more detail for the core level peaks. For example, the narrow scan of the In 3d photoemission peak in Fig. 2.2 (b) shows a doublet structure. Such a splitting is observed for electrons coming from p, d, f, ... orbitals, that is from orbitals with angular momentum quantum number l greater than zero (i.e. l = 1,2,3...). The splitting originates from the spin-orbit coupling interaction, which results in the energy for j = l + s being different from j = l - s, where s (= 1/2) is the electron spin quantum number. The components of the doublet are therefore distinguished by the total angular momentum quantum number j, whose values are: 1/2 and 3/2 for p orbitals, 3/2 and 5/2 for d orbitals, and 5/2 and 7/2 for f orbitals. The intensities of these components are proportional to their respective degeneracies, 2j + 1. Narrow scan spectra may also provide information about the specific chemical state. For example, if an electronegative species like oxygen or fluorine is bonded to carbon, the electron distribution at C becomes changed as this atom assumes a partial positive charge. In turn this results in an increase in the C 1s binding energy, and a “chemical shift” is seen between that C atom and one bonded to less electronegative atoms. For example, for carbon bonded to carbon or hydrogen (C-C, C-H) the C 1s binding energy is very close to 285.0 eV, while a carbon which is single bonded to an oxygen atom (C-O) has a binding energy of 286.5 eV, a carbon double bonded to oxygen (C = O) is at 288.0 eV, and carbon bonded to fluorine (C-F) is around 292.0 eV [73,80,82]. A similar chemical shift effect operates to distinguish between signals from metal and metal oxide in a metallic sample covered by a thin oxide film.
Figure 2.2  (a) A low resolution XPS spectrum for ITO sample and (b) a high resolution In 3d spectrum excited by Al Kα.
2.1.2 Quantitative Analysis

Quantitative analysis with XPS depends on making measurements of peak intensity; this can be defined by the area of the peak left after removing any background contribution. A number of factors contribute to the measurement including the X-ray flux ($f$), the photoelectron cross section ($\sigma$), the number of atoms per unit volume ($n$), the area of the sample from which the photoelectrons are collected ($A$), the instrumental transmission function ($T$) and the inelastic mean free path ($\lambda$) \cite{74}. The inelastic mean free path, $\lambda$, represents the average distance through which the photoelectron can travel in the solid before it undergoes some inelastic scattering. It depends on the electron energy and the nature of the sample. Empirical values of $\lambda$ for elements, inorganic and organic compounds have been tabulated by Seah and Dench \cite{83}, but often for the energy range 100 - 1000 eV, $\lambda$ is around 6 to 20 Å. Sometimes a sampling depth is defined as the depth from which 95% of the signal is contributed to a sharp peak after background correction (this corresponds to $3\lambda$).

The intensity contribution from an infinitesimal thickness $dx$ in a sample \cite{84} (Fig. 2.3) considering the factors listed above is:

$$dl = f \sigma n A T \exp\left(-\frac{x}{\lambda}\right) dx$$  \hspace{1cm} (2.3)

Integration for a semi-infinite homogeneous sample from $x = 0$ to $x = \infty$ gives:

$$I = f \sigma n A T \lambda$$  \hspace{1cm} (2.4)

For a particular peak under study, and particular instrumental settings, $f$, $\sigma$, $A$ and $T$ can be conveniently grouped into a sensitivity factor ($S$), for which relative values are often available (as is the case for measurements with our MAX200 spectrometer). Then the composition ratio for two elements in a sample can be expressed as:

$$n_1/n_2 = \left[\frac{I_1}{S_1}\right]/\left[\frac{I_2}{S_2}\right] \left[\frac{\lambda_2}{\lambda_1}\right]$$ \hspace{1cm} (2.5)
Specific values of $\lambda_1$ and $\lambda_2$ may be used in a quantitative analysis, but for semiquantitative work, the ratio $\lambda_2/\lambda_1$ is commonly taken as constant and equal to unity. Then the elemental composition ratio $n_1/n_2$ within the depth probed can be estimated directly from measured peak intensities and sensitivity factors. This can be generalized for more than two components, when atomic percentages can be expressed as:

$$n_1 \text{ atomic } \% = \left\{ \frac{I_1}{S_1} / \sum_j \frac{I_j}{S_j} \right\} \times 100 \% \quad j = 1,2,3... \quad (2.6)$$

Information on the variation of composition with depth can be obtained by measuring peak intensity as a function of collection angle from the surface [74].

2.2 Instrumentation

2.2.1 Ultrahigh Vacuum System

Fig. 2.4 illustrates the Leybold MAX200 spectrometer which operates in our laboratory. It consists of four interlinked chambers: the transfer chamber (for sample introduction), the
Figure 2.4  A schematic diagram of the MAX200 system viewed from top.
analysis chamber (for performing the analytical measurements), and two preparation chambers for ‘in situ’ sample treatment. The X-ray source, energy analyzer with lens system and detector, as well as the ion gun for sample cleaning and electron gun for Auger analysis are accommodated in the analysis chamber. The sample transferring system consists of an automatic transfer rod for taking a sample from the transfer chamber to the analysis chamber; additionally there are two manual rods for sample transfer from the preparation chambers to the analysis chamber [84].

The spectrometer is designed to operate in the ultrahigh vacuum (UHV) pressure range \(10^{-8} - 10^{-10}\) mbar. This is necessary for two reasons: (i) to prevent low energy electrons from being scattered by residual gas molecules and thus to limit noise in a measured spectrum; and (ii) to limit contamination of the sample surface by adsorption from the residual gas.

UHV conditions are achieved with a pumping system shown schematically in Fig. 2.5. The main chamber is pumped by a combination of pumps, specifically rotary and turbomolecular pumps with an auxiliary titanium sublimation pump. There is also an ion pump present for the X-ray source. UHV systems need to be baked from time to time in order to slow down outgassing by removing adsorbed layers from the chamber walls; in practice for the MAX200 this is done at around 100-120 °C for up to 24 h. After such a baking, the base pressure can be obtained at around \(2 \times 10^{-10}\) mbar for the analysis chamber although during use the pressure is often slightly higher (e.g. \(5 - 8 \times 10^{-10}\) mbar); the typical pressure in the transfer chamber is about \(2 \times 10^{-8}\) mbar.

### 2.2.2 Sample Handling

Samples for analysis are mounted on standard sample holders by using double stick copper tape, and the holders are placed in the transfer chamber. After closing the door, the pressure in this chamber is reduced by the combination of rotary and turbomolecular pumps to
Figure 2.5  Schematic representation of the pumping system for the MAX200.
the 10^{-8} \text{ mbar range}. After that, the sample is moved to the analysis chamber by the automatic transfer rod (which moves in x-direction) where the sample holder locks to the manipulator (PTM 60) dock. Subsequently the automatic transfer rod is moved back to the transfer chamber and the gate valve between the analysis and transfer chambers is closed. The PTM 60 manipulator dock can move a sample in any of the three linear directions (x,y,z), as well as rotate it around two axes, one perpendicular to the sample surface (z-direction) and the other parallel to the sample surface (y-direction), in order to position the sample properly with respect to the X-ray source and collector lens system of the energy analyzer.

### 2.2.3 X-ray Source

X rays are produced by bombarding the anode material with electrons accelerated through a potential difference of about 10 kV from the filament (at ground potential). The electron impact creates core holes in the target, and the relaxation process dominantly involves photon emission. Different anode materials have characteristic emission lines with different energies. The MAX200 spectrometer is equipped with a dual anode X ray source (Fig. 2.6) which gives the Kα line of either Al (1486.6 eV) or Mg (1253.6 eV). Two separate filaments placed near each anode face are connected to the external circuit and switching the power from one to the other, enables the choice of the target material. The anode is water cooled to prevent failure due to heat generation during operation. The radiation generated passes through a thin Al (~ 2 \mu m) window which protects the sample from bombardment by the high energy electrons and Bremsstrahlung radiation that may otherwise degrade the sample. This window also helps reduce the intensity of the additional X-ray lines Kα_{3,4} and Kβ which can add satellite structure in XPS spectrum (low intensity, broad peak at lower binding energy side of a photoelectron peak). These
contributions are not usually a problem but they can be removed by using the monochromator which is available if higher energy resolution is needed.

![Dual anode X-ray source diagram](image)

**Figure 2.6** Dual anode X-ray source.

### 2.2.4 Energy Analyzer

Fig. 2.7 outlines the analyzer system of the MAX200 spectrometer; the main components are the collection lens, the energy analyzer and the multichannel plate detector. The two-stage input lens system controls the collection and focusing of photoelectrons toward the energy analyzer slit by ramping voltages on the different lens elements. The first stage controls the analysis area (spot size) and collection angle for the electrons coming from the sample surface.
Figure 2.7  Schematic diagram for the concentric hemispherical analyzer (CHA) and lens system in the MAX200.
The second stage acts to retard the electron energy to a particular pass energy required for the energy analyzer and it also controls the angle ($\alpha$) at which electrons enter the analyzer.

The concentric hemispherical analyzer (CHA) is constructed from two concentric hemispheres of radius $R_1$ (inner) and $R_2$ (outer) to which a potential difference $\Delta V$ is applied. Electrons travel on the central circular trajectory through the energy analyzer and reach the detector only if their kinetic energy $E_0$ inside the analyzer (the pass energy) satisfies

$$e\Delta V = E_0 \left( \frac{R_2}{R_1} - \frac{R_1}{R_2} \right) \quad (2.7)$$

Therefore, for different $\Delta V$ applied, different pass energies are required. The relative analyzer resolution ($\Delta E_{\text{analyzer}}/E_0$) is a function of the aperture size, the electron entrance angle, and the electron trajectory radius ($R_0$), but this is constant for given analyzer settings. Therefore, a lower pass energy gives a better energy resolution, but this is offset by a reduction in the signal intensity. To obtain an optimum balance between resolution and intensity, an appropriate pass energy should be chosen for each measurement. In this work, a pass energy of 192 eV is used for survey scans while 96 eV is used for narrow scans.

The energy resolution for a peak in a measured spectrum is expressed by the full-width-at-half-maximum (FWHM) height. This measurement contains contributions from the analyzer ($\Delta E_{\text{analyzer}}$), the natural line width of the X-ray source ($\Delta E_{\text{source}}$), as well as the inherent line width of the atomic level involved ($\Delta E_{\text{line}}$). The observed peak width can be expressed by:

$$\Delta E_{\text{peak}} = (\Delta E_{\text{analyzer}}^2 + \Delta E_{\text{source}}^2 + \Delta E_{\text{line}}^2)^{1/2} \quad (2.8)$$

provided all contributions have the Gaussian form [73].

The measured kinetic energy of an electron emitted from a solid sample is referenced to the vacuum level of the spectrometer, while the binding energy of the electron inside the sample is referenced to the Fermi energy of the sample ($E_b$). These energy values are schematically
illustrated in Fig. 2.8. For a conducting sample in electrical contact with the spectrometer, the Fermi levels of sample and spectrometer are equal, and Eq.(2.1) can be re-expressed as:

\[ E_{bf} = h\nu - E_k - \phi_{sp} \]  

(2.9)

where \( \phi_{sp} \) is the spectrometer work function. In practice, \( \phi_{sp} \) can be determined by calibration with a measurement on a standard gold sample, given that the binding energy of the Au 4f\textsubscript{7/2} line can be referenced to 84.0 eV [73,74]. Insulating samples require an internal reference, and the C 1s peak associated with hydrocarbon C-C and C-H bonds at 285.0 eV is commonly used. In this work, as noted in Chapter 3, there can be an overlap with other species; then Ru 3d\textsubscript{5/2} at 280.9 eV is used as a secondary reference.

2.2.5. Data Processing

To maximize the information from XPS spectra, some processing of the raw measured data is required. The first step is to remove the background contribution from the overall measured peak. This work used the nonlinear, background correction introduced by Shirley [86], and this is discussed in relation to Fig 2.9. This method assumes that the number of inelastically scattered electrons at any point in a spectrum is proportional to the number of elastically scattered electrons at higher kinetic energies. This correction (over the energy range chosen by operator) is determined by the iterative algorithm:

\[ N'_{k+1}(E) = N(E) - N(E_{max}) - C \int_E^{E_{max}} N'_k (E) \, dE \]  

(2.10)
$\phi_s = \text{work function of sample (i.e. energy difference between Fermi level and vacuum level)}$

$E_k = \text{kinetic energy of photoelectron with respect to vacuum level of sample}$

$E_b = \text{binding energy of electron in solid with respect to Fermi level}$

$\phi_{sp} = \text{work function of spectrometer}$

$E_{k'} = \text{kinetic energy of photoelectron measured by spectrometer}$

**Figure 2.8**  Schematic diagram of the relevant energy levels for the binding energy measured by spectrometer.
where \( N(E) \) is the measured count rate, \( N'_k(E) \) represents the count rate after subtraction of background contribution (\( k^{th} \) iteration), \( C \) is a constant and \( N(E_{\text{max}}) \) is the reference background level. The process starts with \( N'_1(E) = 0 \) and continues until \( N'_{k+1}(E) \sim N'_k(E) \) which generally requires three or four iterations.

After the background is subtracted from a high-resolution spectrum, a curve fitting process is used to identify all individual overlapping components with regard to peak position, intensity and peak width (FWHM). To optimally apply the fitting method, chemical knowledge of the system has to be connected to the mathematical approach. From the chemistry, a realistic estimate can be made for the number of different chemical components for the element of interest. An example of the curve fitting process is illustrated in Fig 2.10 for a C 1s spectrum measured from Nafion. It is immediately seen that this spectrum has two dominant peaks: an intense broad one at around 292.0 eV, which is assigned to contributions from carbon bonded to fluorine (\( \text{CF, CF}_2, \text{CF}_3, \text{>CF-O-CF}_2 \)), and a less intense peak at around 285.0 eV, which is assigned to hydrocarbon (i.e. \( \text{C-C, C-H} \)) bonding (Fig. 2.10 a). After fitting components at those two positions, it is clear that the level of correspondence between the measured and simulated curves is less than adequate. Additional components must be added, and that has been done in Fig. 2.10 (b). Components have been added at 286.5 eV (C-O bonding) and at 288.0 eV (C=O bonding), contributions which originate from surface oxidation and contamination. In this research, even more complicated cases are present such as overlapping C 1s and Ru 3d signals in spectra measured for Nafion with ion exchanged Ru\(^{2+}\) complex (Chapter 5).

The mathematical approach is to simulate a measured spectrum (after subtraction of background) by a set of individual components, and for each of these the computer processing program available with the MAX200 spectrometer uses the mixed Gaussian and Lorentzian
Figure 2.9 Shirley non-linear background subtraction applied to a Mg 2p narrow scan spectrum.
Figure 2.10  Narrow scan spectrum for C 1s signal in Nafion sample: (a) unfitted and (b) after fitting to different components.
functional form:

\[ f(E) = \frac{\text{peak height}}{[1 + M (E - E_0)^2 / \beta^2]} \exp\{(1-M) \ln 2 (E - E_0)^2 \beta^2\} \]  \hspace{1cm} (2.11)

where \( E_0 \) is the energy for the maximum of the individual component peak, \( \beta \) fixes the width of the component and \( M \) is the mixing ratio (1 for pure Lorentzian; 0 for pure Gaussian). After an initial estimation of these parameters, for all components needed to fit a spectrum, the program multiply iterates to optimize the fit between the simulated spectrum and the measured spectrum. This involves minimizing the least-squares function (\( \chi \)):

\[ \chi = \frac{1}{N_{\text{free}}} \sum_j \left( \frac{Y_{\text{mea},j} - Y_{\text{fit},j}}{Y_{\text{mea},j}} \right)^2 \]  \hspace{1cm} (2.12)

where \( Y_{\text{mea},j} \) is the measured count rate at the \( j \)-th data point, \( Y_{\text{fit},j} \) is the corresponding value of the simulated function obtained as a sum of functions of the type in Eq. (2.11); \( N \) is the number of data points and \( N_{\text{free}} = N - N_{\text{fit}} \) where \( N_{\text{fit}} \) is the number of parameters to be fitted through the minimizing process. Visual comparison of the measured and simulated curves is still important, particularly to ensure that components added fit reasonable chemical criteria.
3.1 Sample Preparation

Samples for XPS characterization were prepared according to the following procedures: panels of ITO (Delta Technologies Limited) were cut to dimensions 15 mm x 5 mm and ultrasonically cleaned for 12 min in water with detergent. This was followed by rinsing with distilled water, and then ultrasonically cleaning for 12 min in methanol, 12 min in acetone and finally air drying at room temperature.

The PPV film (I) was prepared in Prof. Mike Wolf’s laboratory (UBC) by thermal conversion of a thin film of soluble undialyzed and dialyzed sulfonium precursor polymer (II) prepared from α,α'-dichloro-p-xylene (III) in methanol solution. The procedure is illustrated in Fig. 3.1 [87]. The precursor polymer was spin-coated on ITO substrates and air dried at room temperature for 1 h prior to the thermal conversion around 250 °C under vacuum (10⁻³ mbar) for 12 h. After samples had cooled to room temperature, they were transferred into the introduction chamber of the MAX200 facility for surface analysis.

Nafion samples were prepared by deposition of 4 drops of 2.5% solution of Nafion® perfluorinated ion-exchange powder in methanol (Aldrich Chemical Company, Inc.) directly on to clean ITO substrate, followed by drying in air (1 h) and under vacuum (10⁻³ mbar for 1 h) at room temperature before transfer to the XPS facility. The ion exchange of Ru(bpy)₃²⁺ into the Nafion layer was done by dipping the samples of Nafion-coated ITO in aqueous solution of 3 mM Ru(bpy)₃²⁺ for 30 min. After that, the samples were dried for 2 h under vacuum (10⁻³ mbar).
Figure 3.1  Schematic presentation of PPV synthesis.
For the two-layer structure device (Mg/Nafion + Ru(bpy)$_3$$^{2+}$/PPV/ITO), two drops of Nafion (2.5% in methanol solution) were deposited on top of PPV-coated ITO. The samples were air dried at room temperature, and Ru(bpy)$_3$$^{2+}$ ions were incorporated as described above.

For the diode fabrication, it is necessary to etch small regions on the ITO substrate prior to polymer deposition in order to prepare the structure as indicated in Fig. 3.2. Etching was done by placing a small amount of Zn powder on exposed ITO surface (area 4 mm x 4 mm) and adding the few drops of 10% HCl. The rest of the sample area was protected by scotch tape. After 5 min, the sample was rinsed with distilled water and the cleaning procedure was applied. The removal of the ITO layer from the etched region was confirmed by measuring the electrical resistance.

Figure 3.2 Diode fabrication: (a) etched ITO substrate and (b) after polymer and metal deposition.
3.2 High Vacuum System for PLED Preparation

To fabricate a PLED, metal has to be deposited on top of the polymer film which has been previously applied to the ITO substrate (Fig. 3.2 b). In this work, magnesium was deposited by thermal evaporation under high vacuum (HV) conditions. Figure 3.3 illustrates the HV system designed and built for this purpose. The stainless steel chamber has double walls which enable water cooling during the metal deposition. The chamber is equipped with an evaporation source, and an ion gauge (Varian, UHV-24 2.75") with two thoria-coated-iridium filaments for pressure measurement. The base pressure of the chamber is $2 \times 10^{-5}$ mbar, which is achieved by a diffusion pump (Edwards, EO2K, air pumping speed 150 L/s). The manipulator rod, with sample holder at its end, can rotate and translate the sample along the “x” direction (see Fig. 3.3). Tantalum foil is used to cover that part of the sample which must be protected from the metal deposition.

The design of the metal evaporation source is illustrated in Fig. 3.4. A narrow quartz tube (length 2 cm, outer diameter 4 mm) with one end closed is filled with magnesium turnings (Johnson Matthey) and wrapped with tungsten wire, which is attached to the copper feedthroughs. Evaporation of Mg is achieved by applying current through the W wire from the transformer. Before each evaporation, the source was outgassed for 45 min at a current of 1.5 A. Then, the sample was positioned in front of the evaporation source (distance 3 cm) and current was gradually increased up to 3 A and maintained at that value for 5 - 10 min depending on the desired Mg film thickness. When sufficient metal has been deposited, the sample was moved back from the evaporation source and kept under vacuum ($10^{-3}$ mbar) for 2 h, to allow cooling under vacuum. The samples prepared for surface analysis were then transferred into the XPS facility. Other samples, prepared for electroluminescence testing, were placed in a nitrogen box and connected to a current supply (Anatek Electronics LTD). A three-terminal adjustable-current
Figure 3.3  Design of high vacuum system for PLED preparation.
power regulator (LM 317) designed in UBC chemistry electrical shop was used to provide a controlled constant current in the range to 100 mA across the device.

Figure 3.4 Design of evaporation source.

3.3 Sample Characterization

Samples were characterized with XPS in the Leybold MAX200 spectrometer, where the pressure of the analysis chamber at the time of a measurement was typically $5 \times 10^{-9}$ mbar, and photoelectrons were collected from a sampling area of 2 mm x 4 mm. The unmonochromatized Al Kα source (1486.6 eV) was operated at 10 kV and 20 mA. Survey scans were measured with a pass energy of 192 eV, while higher resolution spectra were measured at a pass energy 96 eV.

Spectra from polymer samples were generally calibrated according to the position of C 1s hydrocarbon peak at 285.0 eV binding energy. In the situation where Mg was evaporated on to a Nafion + Ru(bpy)$_3$$^{2+}$ layer, this C 1s signal could be obscured by overlapping components. In that case, the Ru 3d$_{5/2}$ peak at 280.9 eV binding energy was chosen as a secondary reference.
This was determined by studies on Nafion + Ru(bpy)$_3^{2+}$ samples where binding energies could be calibrated with respect to the C 1s reference signal.
Chapter 4  Studies of Interfaces in Mg/PPV/ITO Diode

4.1  XPS Studies of Undialyzed PPV Film on ITO Substrate

The low resolution spectrum of PPV film on ITO substrate illustrated in Fig. 4.1 shows a series of photoelectron peaks at characteristic binding energies for Na 1s, O 1s, C 1s, Cl 2p, Si 2s, Si 2p, Na 2s, O 2s and Auger signals for C (KLL), O (KVV) and Na (KLL). The relative atomic composition according to XPS is given in Table 4.1. The small amounts of Na, Cl and Si apparently represent impurities introduced during the polymer synthesis. Similar observations were reported by Obrzut and Karasz [49] in one of the first XPS characterizations of PPV.

Table 4.1  Relative atomic compositions for PPV film deduced from spectrum in Fig. 4.1

<table>
<thead>
<tr>
<th>element</th>
<th>C</th>
<th>O</th>
<th>Na</th>
<th>Cl</th>
<th>Si</th>
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<td>atomic %</td>
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<td>10.9</td>
<td>0.6</td>
<td>1.4</td>
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</table>

Figure 4.2 shows the C 1s high resolution spectrum. The peak is not symmetric, and this suggests the presence of more than one component. The fitted spectrum in Fig. 4.3 (a) shows two components: an intense component at 285.0 eV binding energy (FWHM equal to 1.5 eV), which is assigned to the aromatic and aliphatic parts of the molecule, and a smaller component at 286.5 eV (FWHM equal to 1.8 eV) assigned to the C-O (alcohol or ether) contributions. The latter represents 16% of the total C 1s signal and is believed to originate from some polymer oxidation. Kobryanskii et al. [87] have reported that methoxy groups and C=O bonds can form in the polymer chain when the sulfonium precursor PPV polymer is stored at 0-5 °C. This affects the electronic and physical structure of the polymer. The appearance of C-O in this work may
Figure 4.1 XPS survey spectrum from PPV on ITO sample.
Figure 4.2  C 1s spectrum for PPV.
Figure 4.3  (a) Fitted C 1s spectrum and (b) O 1s spectrum in PPV.
arise for a similar reason. Papadimitracopoulos et al. reported evidence from FTIR spectroscopy for carbonyl group formation during the thermal conversion of PPV [88], but our results do not show the presence of any structure at a characteristic binding energy that could be taken as indicative of carbonyl. The low-intensity broad peaks at 291.0 eV and 294.1 eV (Fig. 4.2) represent $\pi-\pi^*$ shake-up satellites associated with the aromatic rings [73], but they have probably been reduced by some surface oxidation.

The O 1s spectrum illustrated in Fig. 4.3 (b) shows a main peak at 533.3 eV (FWHM equal to 1.85 eV) which has been assigned to oxygen from hydroxyl (C-OH) and ether groups (C-O) [89] associated with oxygen impurities and defects in the polymer chain. Xing et al. reported that some of these oxygen impurities can be removed by heating the polymer under UHV conditions, and the removable component was assigned to a weakly bound form of oxygen [90].

### 4.2 XPS Studies of Mg/undialyzed PPV Interface

The XPS survey spectrum measured after the deposition of Mg on PPV film under high vacuum conditions is illustrated in Fig. 4.4. Photoelectron signals were observed at characteristic binding energies for Mg 1s, Na 1s, O 1s, C 1s, Cl 2p, Mg 2s, Mg 2p, and Auger signals are recognized for C (KLL), O (KVV), Na (KLL) and Mg (KLL). The relative atomic composition is given in Table 4.2. Impurities such as Na and Cl are still detected, but the dominant changes from the addition of Mg, are the considerable increase in the relative amount of O and the decrease for C.
Figure 4.4  XPS survey spectrum from PPV with evaporated Mg.
Table 4.2 Relative atomic compositions for Mg/PPV sample deduced from spectrum in Fig. 4.4

<table>
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<th>C</th>
<th>O</th>
<th>Na</th>
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<tr>
<td>atomic %</td>
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<td>39.2</td>
<td>1.1</td>
<td>1.2</td>
<td>33.3</td>
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</tbody>
</table>

The C 1s spectrum after Mg deposition is shown in Fig. 4.5 (a). A second main component is now present compared to the situation for the spectrum from PPV alone (Fig. 4.2), but the asymmetry apparent in the two peaks after the deposition of Mg indicates the presence of overlapping subcomponents. A curve fitted spectrum is shown in Fig. 4.5 (b). The high intensity peak at 285.0 eV (FWHM equal to 1.8 eV) arises from the C-C and C-H contributions in PPV, but its overall intensity has decreased by 74% compared with the similar component before the Mg deposition. The component in C 1s spectrum at 286.4 eV binding energy (FWHM equal to 1.8 eV) represents the C-O component and its intensity is 10% of the total C 1s intensity. New components are present at the higher binding energies of 288.7 eV and 289.8 eV (FWHMs equal to 1.8 eV), and they are assigned to carbon bonded in the carbonyl C=O and carboxylic O-C=O groups respectively. They represent 10.5% and 15% respectively of the total C 1s signal. These changes observed after Mg deposition are similar to the results obtained by Johansson et al. [91] upon depositing indium-tin oxide on PPV under high vacuum conditions, as well as to the changes reported after PPV is photo-oxidized [92], and they are believed to correspond to the PPV being partially oxidized. The component at 284.0 eV (FWHM equal to 1.8 eV), which represents 6% of the total C 1s signal, is assigned to the carbon interacting directly with the deposited Mg (i.e. to Mg-C formation). This contrasts with a report based on theoretical calculations [93] according to which it was concluded that Mg should not react with the conjugated backbone. However those quantum-mechanical calculations were performed on
Figure 4.5  C 1s spectrum from PPV after Mg deposition: (a) raw spectrum and (b) after curve fitting process.
polyacetylene and did not take into account the presence of some oxygen defects in the polymer chain, as well as some polymer surface oxidation. Table 4.3 illustrates the relative ratios of different carbon components before and after Mg deposition. It appears that the amount of the C-O component decreases after Mg deposition, but other higher oxidized components form as well, and there is some carbide interaction.

Table 4.3 Relative amounts according to XPS of different carbon components before and after Mg deposition on PPV

<table>
<thead>
<tr>
<th>components</th>
<th>ratio before Mg</th>
<th>ratio after Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (C-O) / C (285.0 eV)</td>
<td>0.19</td>
<td>0.17</td>
</tr>
<tr>
<td>C (C=O) / C (285.0 eV)</td>
<td>-----</td>
<td>0.18</td>
</tr>
<tr>
<td>C (O-C=O) / C (285.0 eV)</td>
<td>-----</td>
<td>0.26</td>
</tr>
<tr>
<td>C (C-Mg) / C (285.0 eV)</td>
<td>-----</td>
<td>0.10</td>
</tr>
</tbody>
</table>

The O 1s spectrum after Mg evaporation is illustrated in Fig. 4.6 (a); there are considerable changes compared with the situation for PPV alone. There is a net increase in peak intensity, and that suggests oxygen impurities are introduced during the metal deposition. Three overlapping components can be distinguished. The component of highest intensity at 532.2 eV binding energy (FWHM equal to 1.9 eV) is assigned to oxygen from the C=O and O-C=O groups, the component at 533.3 eV (FWHM equal to 1.9 eV) belongs to oxygen single bonded to carbon (i.e. C-O), while the component at 530.4 eV (FWHM equal to 2 eV) is interpreted as the signal of oxygen bound to Mg. These components represent respectively 60%, 21% and 19% of the total O 1s intensity. The components at 532.2 eV and 530.4 eV are not seen prior to the Mg deposition on PPV.
Figure 4.6  XPS spectra for PPV after Mg deposition: (a) O 1s and (b) Mg 2p.
Figure 4.6 (b) represents the measured Mg 2p spectrum. The broad peak contains two overlapping components. The higher binding energy component at 49.0 eV (FWHM equal to 2.5 eV) is assigned to the metal oxide signal while the lower binding energy component at 48.2 eV (FWHM equal to 1.6 eV) represents the metallic peak. The oxide component has a greater area by a factor of 2.7 over the metallic component, and that indicates for our depositing conditions that the oxidized form dominates. The very broad oxide peak will also indicate contributions from the Mg-C interaction.

4.3 XPS Studies of Dialyzed PPV and Its Interface With Mg

When the precursor polymer of PPV is dialyzed, it becomes purified from impurities and low molecular polymer masses which can exist in oxidized form. Therefore it may not be surprising that this dialysis can affect the purity and chemical state of the PPV polymer formed after temperature conversion of the precursor. Figure 4.7 shows a survey spectrum measured for PPV film on ITO made from dialyzed precursor polymer. Photoelectron peaks from C 1s, O 1s, Si 2s and Si 2p are present as well as Auger signals C (KLL) and O (KVV). The relative atomic compositions deduced from the survey spectrum correspond to C 91.6% and O 6.1% and Si 2.3%, and this indicates a much smaller involvement by oxygen compared with PPV formed from the undialyzed precursor (see Table 4.1), but still a small amount of Si impurity is present.

Figure 4.8 (a) shows the high resolution C 1s spectrum measured for the dialyzed PPV film. Two components can be distinguished; the main component at 285.0 eV (FWHM equal to 1.4 eV) is assigned to C-C, C-H, and the minor component at 287.4 eV (FWHM equal to 1.8 eV) is assigned to C=O, which represent 3% of the total carbon signal. Contribution by C-O was not detected in this case.
Figure 4.7  XPS survey spectrum measured from dialyzed PPV sample.
Figure 4.8  High resolution spectra for dialyzed PPV: (a) C 1s and (b) O 1s.
The O 1s spectrum illustrated in Fig. 4.8 (b) shows two components. The intense component at 532.6 eV binding energy (FWHM equal to 1.7 eV) belongs to oxygen from hydroxyl groups, while the component at 533.8 eV (FWHM equal to 1.7 eV) is assigned to oxygen from O-C=O groups and it represents 11% of the total oxygen signal. These results obtained for the PPV prepared under low vacuum conditions (e.g. 10^{-3} mbar) are consistent with observations reported by Hsieh et al. [53], who also noticed the presence of the carboxylic group component in the O 1s spectrum when the preparation of PPV was done under argon atmosphere and in UHV.

The XPS survey spectrum measured after Mg deposition on dialyzed PPV film under high vacuum conditions is illustrated in Fig. 4.9. Photoelectron peaks from Mg 1s, C 1s, O 1s, Mg 2s and Mg 2p are seen at the characteristic binding energies as well as Auger signals from C (KLL), O (KVv) and Mg (KLL). No impurities were detected. The relative atomic compositions calculated from the spectral peak areas are given in Table 4.4. The C 1s signal decreases markedly, and the O 1s signal increases, compared with the initial situation noted at the beginning of this section.

Table 4.4 Relative atomic compositions for Mg/dialyzed PPV sample deduced from spectrum in Fig. 4.9.

<table>
<thead>
<tr>
<th>element</th>
<th>C</th>
<th>O</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>atomic %</td>
<td>41.9</td>
<td>29.2</td>
<td>28.9</td>
</tr>
</tbody>
</table>

The C 1s spectrum after Mg evaporation is shown in Fig. 4.10. The situation is considerably different from the effect of Mg deposition on the undialyzed PPV film. Now two high intensity components dominate, and these are the components at 285.0 eV (C-C, C-H) and
Figure 4.9 XPS survey spectrum measured from dialyzed PPV after Mg deposition.
Figure 4.10  C 1s spectrum for Mg/dialyzed PPV sample.
at 287.4 eV (C=O) (both have a FWHM equal to 1.8 eV). Other components are less intense and are located at 286.5 eV (C-O), 289.0 eV (O-C=O) and 291.2 eV; these components also have FWHMs equal to 1.8 eV. The component at 291.2 eV binding energy must involve C bonded in a highly oxygenated species; in the following, this is referred to as carbonate although we do not at this time have independent evidence for the presence of this ion. The relative amounts of the different carbon components before and after the Mg evaporation on dialyzed PPV are presented in Table 4.5. Compared to the corresponding values measured from undialyzed PPV after Mg deposition (Table 4.3), the C=O component is now more intense than that for C-O, the C-Mg interaction is negligible and a new component associated with carbonate is present.

Table 4.5 Relative amounts for different carbon components identified in C 1s spectra measured from dialyzed PPV before and after Mg evaporation

<table>
<thead>
<tr>
<th>components ratio</th>
<th>before Mg</th>
<th>after Mg</th>
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<tbody>
<tr>
<td>C_(C-O) / C_(285.0 eV)</td>
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<td>0.21</td>
</tr>
<tr>
<td>C_(C=O) / C_(285.0 eV)</td>
<td>0.03</td>
<td>0.46</td>
</tr>
<tr>
<td>C_(O-C=O) / C_(285.0 eV)</td>
<td>-----</td>
<td>0.08</td>
</tr>
<tr>
<td>C_(carbonate) / C_(285.0 eV)</td>
<td>-----</td>
<td>0.09</td>
</tr>
</tbody>
</table>

The O 1s spectrum after Mg deposition (Fig. 4.11 a) shows changes compared to the situation with dialyzed PPV alone (Fig. 4.8 b). Two overlapping components with relatively equal areas can now be fitted. The broad component at 532.2 eV binding energy (FWHM equal to 2.4 eV) is believed to contain contributions from both C=O and oxygen from Mg oxide formed at the dialyzed PPV surface after the Mg deposition. The component at 533.8 eV
Figure 4.11  High resolution spectra for Mg/dialyzed PPV: (a) O 1s and (b) Mg 2p.
(FWHM equal to 2.3 eV) then contains contributions from oxygen in C-O, O-C=O and carbonate groups.

Figure 4.11 (b) illustrates the Mg 2p spectrum with distinguishable oxide and metallic contributions. The oxide component is located at 51.8 eV binding energy (FWHM equal to 2.1 eV), while the metallic component is at 50.6 eV (FWHM equal to 1.9 eV). They have relatively equal areas. Both components are showing different binding energies compared to the similar spectrum from the Mg/undialyzed PPV system. This point needs further checking since it is not absolutely clear whether this change relates to differences in metal growth or whether it arises as an instrumental artifact (e.g. incomplete calibration of energy scale).

The results presented in this Chapter show that Mg deposition on PPV under the high vacuum conditions yields significant oxidation of the polymer surface. Different oxidized carbon components can appear, depending on whether the polymer precursor is dialyzed or not. Dialysis clearly improves the purity of PPV, especially by reducing oxygen contamination (it removes oxidized low mass polymer fragments), but the surface formed still undergoes oxidation upon the deposition of Mg for the conditions used in this work. Study of the Mg/undialyzed PPV interface showed that Mg metallic and oxide peaks appear at lower binding energy than is the case for the Mg/dialyzed PPV sample.
Chapter 5  Studies of Interfaces in

Mg / Nafion + Ru(bpy)$_3^{2+}$ / PPV / ITO Diode

5.1  Introduction

In this work a layer of Nafion® with incorporated Ru$^{2+}$ complex {Ru(bpy)$_3^{2+}$} was placed between PPV and a Mg electrode. The idea was to explore new possibilities for PLED design inspired by the presence of electron withdrawing CF$_3$ and CF$_2$ groups in Nafion and the known properties of Ru$^{2+}$ complexes to exhibit electrogenerated chemiluminescence, a process closely related to electroluminescence.

Although the structure of Nafion® has still not been fully characterized, several models have been proposed to describe the observed properties and selectivities. A widely accepted model is the Yeager Three Phase Model [94], based on a three phase cluster system, with interconnecting channels within the polymer, as illustrated in Fig. 5.1. Region A consists of a hydrophobic fluorocarbon backbone, region C is a hydrophilic clustered region where the majority of the ion exchange sites, counter ions and sorbed water molecules are found, and region B is the interfacial region between A and C, which contains some pendant side chains, some water, sulfate and counter ions which are not in clusters. This microphase separation morphology is believed to be responsible for the specific properties observed for Nafion.

Studies of the interaction between Nafion and Ru(bpy)$_3^{2+}$ (where bpy = 2,2'-bipyridine) have attracted much attention since Rubinstein and Bard [68] reported a new type of polymer-coated modified electrode having a chemiluminescence response. By applying a potential to a pyrolytic graphite electrode, coated with a layer of Nafion with ion exchanged Ru(bpy)$_3^{2+}$ from aqueous solution, an intense orange emission was generated. The new electrodes are attractive
Figure 5.1  (a) Chemical formula of Nafion® and (b) schematic indication of the three phase model.
because of possible catalytic properties [95] as well as applications to the photodetection of oxygen [96]. Examination of the luminescence quenching by different cations present in the water-swollen Nafion membrane [97] indicates that two types of interaction operate between Nafion and Ru(bpy)$_3^{2+}$: electrostatic interaction with sulfonate head groups and hydrophobic interaction with fluorocarbon chains. Prieto and Martin [98] reported a similar conclusion by studying dissolved Nafion in the presence of hydrophobic cations such as methylviologen and Ru(bpy)$_3^{2+}$. However, to our knowledge, no surface science studies have been performed to study the interaction between Nafion and the Ru$^{2+}$ complex.

5.2 XPS Studies of Nafion

The measured XPS survey spectrum for Nafion (Fig. 5.2) shows a series of photoelectron peaks at characteristic binding energies for F 1s, O 1s, C 1s, S 2s, S 2p, and F 2s, as well as Auger signals for C (KLL), O (KVV) and F (KLL).

The comparison between the theoretical and experimental elemental composition is given in Table 5.1. Theoretical data have been obtained from Nafion chemical formula (C$_{20}$F$_{39}$O$_5$S, Mw equal to 1094 g/mol) where hydrogen was excluded from the calculation in order to compare with measured peak areas from XPS. There is an overall satisfactory agreement between the composition data from the different sources. The lower proportion for S seen by XPS suggests that the sulfonate groups are preferentially displaced from the surface toward the bulk.
Figure 5.2  Low resolution XPS spectrum measured for Nafion.
Table 5.1  Relative atomic composition of Nafion from chemical formula and from XPS

<table>
<thead>
<tr>
<th>atomic %</th>
<th>C</th>
<th>O</th>
<th>F</th>
<th>S</th>
</tr>
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<tbody>
<tr>
<td>formula</td>
<td>30.8</td>
<td>7.7</td>
<td>60.0</td>
<td>1.5</td>
</tr>
<tr>
<td>XPS</td>
<td>33.6</td>
<td>6.1</td>
<td>59.7</td>
<td>0.4</td>
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</tbody>
</table>

A measured C 1s spectrum from Nafion is shown in Fig. 5.3 (a). The strong peak at 291.6 eV (FWHM equal to 2.2 eV) is interpreted as arising from the superposition of signals from CF₂, CF-O, CF₂-O groups in the polymer chains [99]. The small component at 293.9 eV (FWHM equal to 1.8 eV) is assigned to CF₃, and its area represents 4.6% of the total CFₓ contribution, which is consistent with the chemical formula of Nafion (see Fig. 5.1 a). Peaks at lower binding energy (FWHMs equal to 1.8 eV) come from contamination: hydrocarbon C-C and C-H at 285.0 eV, C-O at 286.5 eV and C=O at 288.5 eV. These non-fluorine bonded carbon peaks represent 26.4% of the total carbon signal, and come from contamination introduced during the Nafion fabrication. Boiling of Nafion samples in H₂SO₄ for a few hours can help purification [100]. The C/F ratio is observed here to equal 0.56, which is increased a little over the value 0.51 expected from the formula. Straaten-Nijehuis and Sudhölter [101] observed the higher C/F ratio of 0.72, which they explained as due to surface degradation occurring during the X-ray exposure.

The O 1s spectrum in Fig. 5.3 (b) is assigned to the contributions from Nafion. Two overlapping components are distinguishable and this is consistent with previous observations [100]. The lower binding energy component at 533.0 eV (FWHM equal to 2.6 eV) corresponds to oxygen in the SO₃⁻ and SO₄²⁻ groups, while the higher binding energy peak at 535.5 eV (FWHM equal to 2.6 eV) is associated with ether-type linkages (i.e. >CF-O-CF₂⁻) in the
Figure 5.3 High resolution spectra measured for Nafion: (a) C 1s and (b) O 1s.
polymer. The peak widths are relatively broad, which may indicate some overlapping components, including contamination, but the intensity ratio: \( \frac{O_{(SO_3^+ \cdot SO_4^{2-})}}{O_{(\cdot CF-\cdot CF2^-)}} \) equals 0.47, which is close to the expected value of 0.50. Higher values of 0.53 and 0.67 were obtained in other work [100, 101].

The F 1s high resolution spectrum from Nafion (Fig. 5.4 a) shows a broad intense peak at 689.7 eV (FWHM equal to 2.2 eV) and this is fully consistent with previous observations [99].

The S 2p spectrum (Fig. 5.4 b) shows contributions from two overlapping doublet components. The lower binding energy component at 168.5 eV (FWHM equal to 2.0 eV) is attributed to the S from \( SO_3^- \) groups [98] while the higher binding energy component at 170.0 eV (FWHM equal to 1.9 eV) represents the S signal from \( SO_4^{2-} \) ions which are believed to arise from the oxidation of some \( SO_3^- \) groups. The existence of both \( SO_3^- \) and \( SO_4^{2-} \) contributions was reported previously on the basis of an O 1s spectrum [100], but prior to this study no similar assignments have been made from S 2p signals. In our results, the S 2p peak shape cannot be successfully fitted with only one component, giving rise to the conclusion that an additional higher binding energy component is present. The experimentally measured ratio of these two components is \( S_{(SO_3^-)} / S_{(SO_4^{2-})} \) equal to 2.62.

5.3 XPS Studies of Nafion with Ion Exchanged Ru(bpy)$_3^{2+}$

Figure 5.5 shows a survey spectrum measured for a Nafion + Ru(bpy)$_3^{2+}$ system formed on ITO, but it is sufficiently thick that signals from ITO substrate cannot be seen by XPS. Peaks at characteristic binding energies are assigned to photoelectrons from F 1s, O 1s, Ru 3p, N 1s, C 1s, S 2s, S 2p and F 2s, as well as Auger signals for C (KLL), O (KVV) and F (KLL). Comparison with the corresponding spectrum of Nafion in Fig. 5.2 shows additional structure
Figure 5.4  High resolution spectra measured for Nafion: (a) F 1s and (b) S 2p.
Figure 5.5  Low resolution spectrum measured for Nafion + Ru$^{2+}$ complex sample.
arising from the presence of the exchanged Ru$^{2+}$ complex, specifically for the appearance of Ru 3p and Ru 3d photoelectron peaks and the N 1s signal coming from the bipyridine ligands.

The high resolution C 1s spectrum illustrated in Fig. 5.6 is very similar to that obtained from Nafion alone, except that the hydrocarbon component at 285.0 eV is increased by 19%, as a result of the additional carbon contribution from the bipyridine ligands in the Ru$^{2+}$ complex. The Ru 3d spectrum shows a doublet structure with a separation of 4.1 eV between its components. The lower binding energy component Ru 3d$_{5/2}$ is located at 280.9 eV (FWHM equal to 1.7 eV), while the higher binding energy component Ru 3d$_{3/2}$ overlaps with C 1s at 285.0 eV. Other C 1s signals are present as well, including contributions from C-O at 286.6 eV and C=O at 288.2 eV (both FWHMs equal 1.8 eV). The most intense peak at 291.5 eV arises from CFx ($x = 1, 2$) and CFx-O species. This latter peak has FWHM equal to 2.1 eV, which is 0.1 eV narrower than the corresponding component from Nafion alone. The small component at 294.0 eV (FWHM equal to 1.8 eV) corresponds to the CF$_3$ contribution.

A satellite signal from the fluorocarbon component also appears in the C 1s spectrum. It represents contributions from photoelectrons excited by the less intense components of X-ray radiation from the non-monochromatic source [73]. This contribution is located at 281.6 eV binding energy, and it overlaps with the Ru 3d$_{5/2}$ component. The satellite contribution (peak area) is calculated to be 9.8% of total area of CFx signals in C 1s spectra, and this exactly corresponds to the situation for the C 1s spectrum from Nafion alone.

Figure 5.7 (a,b) compares measured S 2p spectra from Nafion and from the Nafion + Ru$^{2+}$ complex sample, while Fig. 5.7 (c,d) presents the same spectra after fitting to particular components. The peaks at 167.5 eV and 169.2 eV (Fig. 5.7 d) are assigned to S from SO$_3$$^-$/ and SO$_4$$^{2-}$ respectively. The intensity of the higher binding energy component does not change on adding the Ru$^{2+}$ complex, but the intensity of the lower binding energy component is increased...
Figure 5.6  C 1s spectrum measured for Nafion + Ru$^{2+}$ complex sample.
by 83% compared to the same component observed from Nafion alone; also this component shows a chemical shift of 1.0 eV to lower binding energy. The ratio $S_{(SO_3^-)} / S_{(SO_4^{2-})}$ is indicated to equal 5.60 for the Nafion + Ru$^{2+}$ complex sample, and this is about twice that from Nafion alone. The observed chemical shift is believed to be due to the electrostatic interaction between Ru(bpy)$_3^{2+}$ ions and the sulfonic groups, while the total increase of the amount of S detected after exposure of the Nafion film to aqueous solution of Ru$^{2+}$ complex is believed to indicate some surface restructuring induced by the hydration and interaction with the Ru(bpy)$_3^{2+}$.

Scherer and Pflunger [100] studied a dried Nafion membrane in the H$^+$ form (in which the sample had been exposed to aqueous media before drying). They noticed an enhanced sulfur concentration at the surface compared to the bulk composition, and these observations were explained in terms of the sulfonic groups being oriented at the surface of a swollen membrane toward the aqueous phase for better hydration. Upon drying, that orientation becomes “frozen” and is observable with XPS. Our results are expressing the same hydrophilic effect, as well as an additional driving force for the orientation of the surface sulfonic groups caused by the interaction with the Ru$^{2+}$ complex.

Figure 5.8 compares O 1s spectra from Nafion and from the Nafion + Ru$^{2+}$ complex sample. Figure 5.8 (b) shows two separated components after the ion exchange with Ru(bpy)$_3^{2+}$. The peak at 535.5 eV, assigned to ether-type links ($>\text{CF-O-CF}_2$) in the polymer, is reasonably constant after the Ru$^{2+}$ complex ion exchange, but the lower binding energy component associated with $SO_3^-$ and $SO_4^{2-}$ shifts by 1.1 eV to the lower binding energy, and its area is increased by 85% compared with that component in the O 1s spectrum from Nafion. The ratio $O_{(SO_3^- + SO_4^{2-})} / O_{(>\text{CF-O-CF}_2)}$ after the Ru$^{2+}$ complex ion exchange is increased to 0.75, compared with the value of 0.47 before the exchange. These results relate to the corresponding changes
Figure 5.7 Comparison of S 2p spectra for Nafion + Ru$^{2+}$ complex samples:
(a) unfitted spectrum from Nafion; (b) unfitted spectrum from Nafion + Ru$^{2+}$ complex; (c) fitted spectrum to show components in (a); and (d) fitted spectrum to show components in spectrum (b).
Figure 5.8  Comparison of O 1s spectra measured from: (a) Nafion and (b) Nafion + Ru$^{2+}$ complex sample.
observed in the S 2p signal, and similarly express the influence of both the electrostatic interaction and some structural rearranging.

Only small changes are observed in the F 1s narrow scan spectrum. The fluorine peak at 689.5 eV has a FWHM equal to 2.0 eV, and this is 0.2 eV narrower than that observed in the spectrum from Nafion alone.

5.4 XPS Characterization of a Nafion + Ru(bpy)$_3^{2+}$ Film Deposited on PPV

The sample discussed in the previous section (i.e. 5.3) represents a thick film of Nafion + Ru$^{2+}$ complex on ITO (this sample is referred to here as sample A). The sample discussed in the present section represents a thin film of Nafion + Ru$^{2+}$ complex on PPV (this is referred to as sample B). The characterization of sample B is important because such an interface exists in a subsequently fabricated diode of type Mg/Nafion + Ru$^{2+}$ complex/PPV/ITO. The interface formed between Mg and the Nafion + Ru$^{2+}$ complex upon metal deposition is studied in Section 5.5. Differences are observed in measurements on sample B compared with those on sample A, and it is believed that these differences arise from the different film thicknesses. The conclusion is that a thin Nafion + Ru$^{2+}$ complex film (sample B) can undergo a greater amount of surface rearrangement than the thicker film (sample A), and this is supported by the following results.

Figure 5.9 compares a measured C 1s spectrum from sample B (thin Nafion + Ru(bpy)$_3^{2+}$ film deposited on PPV) with that from sample A. Although the substrates are different, as far as the XPS probe is concerned the Nafion + Ru(bpy)$_3^{2+}$ parts of samples A and B should be similar except for the effect of film thickness. The intensity of the C 1s component at 285.0 eV is increased by 53% from A to B because the latter contains signals from the PPV underlayer, carbon from Ru$^{2+}$ complex bipyridyl ligands and some hydrocarbon contamination from the Nafion.
Figure 5.9  Comparison of C 1s spectra: (a) sample A (thick Nafion + Ru$^{2+}$ complex film); (b) sample B (thin Nafion + Ru$^{2+}$ complex film on PPV); (c) fitted spectrum (a) to show components.
Fig. 5.10 (a) illustrates the O 1s spectrum from sample B. It exhibits a higher intensity for the component assigned to O from SO$_3^-$ and SO$_4^{2-}$ groups at 532.0 eV binding energy compared to the intensity of the component associated with the ether part of Nafion at 535.5 eV. The ratio measured for $O_{(SO_3^- + SO_4^{2-})}/O_{(CF-O-CF_2)}$ equals 1.59, which is about twice that for the same ratio measured from sample A. This strongly indicates that S-containing groups are oriented much more to the surface in sample B (with the thin film).

The conclusion just given from the O 1s spectrum is reinforced by measurements of the S 2p signal (Fig. 5.10 b). The ratio $S_{(SO_3^-)}/S_{(SO_4^{2-})}$ from sample B is found to equal 12.0. This indicates that sample B has a relatively higher concentration of SO$_3^-$ species in the surface region, and it again supports the concept that more surface rearranging can occur with the thinner film.

5.5 Mg Deposition on the Nafion + Ru(bpy)$_3^{2+}$/PPV/ITO Sample

When Mg is evaporated on top of the sample B (thin Nafion + Ru(bpy)$_3^{2+}$ film on PPV), studied in Section 5.4, significant changes can be observed in the narrow scan spectra for C 1s, O 1s and F 1s.

Figure 5.11 compares C 1s spectra from the original sample (without Mg) with those measured after two different thicknesses of Mg have been added. Changes are visible in the intensities, shapes and binding energy positions for both dominant components. The intensity of the fluorocarbon component (CFx) at 291.4 eV decays more than the hydrocarbon component at 285.0 eV, and exhibits a chemical shift to the lower binding energy side by 0.6 eV. This is interpreted as the Mg primarily interacting with the hydrophobic (i.e. fluorocarbon) part of the polymer. The component at the lower binding energy position (~285.0 eV) decays less, but its shape changes which indicates differences in intensities for the subcomponents. The detailed fit
Figure 5.10 High resolution spectra measured from sample B (thin Nafion + Ru$^{2+}$ complex film on PPV): (a) O 1s and (b) S 2p.
Figure 5.11 Comparison of C 1s spectra measured from: (a) Nafion + Ru$^{3+}$ complex thin film on PPV; (b) sample in (a) after deposition of Mg thin film; (c) sample in (a) after deposition of more Mg (i.e. to form thicker film).
of the spectrum in Fig. 5.11 (c) is illustrated in Fig. 5.12 (a). Two new components appear at 289.6 eV and 283.8 eV, and they are assigned respectively to carbon from the carboxyl group (O=C-O) and carbon bonded to Mg (C-Mg). This indicates that some interfacial oxidation occurs upon Mg deposition, and suggests that Mg interacts with hydrocarbon impurity on the surface to form a carbide type of linkage. The component associated with carbon singly bonded to oxygen (i.e. C-O), originally present at 286.5 eV, shifts to 285.9 eV, presumably due to the C-O-Mg interaction. Table 5.2 gives data for the intensity ratios of different carbon components before and after Mg deposition. The dramatic increase in the $C_{(C=O)}/C_{(285 \text{ eV})}$ ratio indicates an increase in surface oxidation upon using the Mg evaporation source in high vacuum conditions. Ratios of different carbon components compared to the intensity of fluorocarbon component (CFx) also are increased after Mg.

Table 5.2  Relative intensities of different carbon components in samples before and after Mg deposition on the Nafion +Ru(bpy)$_3^{2+}$/PPV sample

<table>
<thead>
<tr>
<th>ratio of components</th>
<th>before Mg</th>
<th>after Mg (thick layer)</th>
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<td>$C_{(C-O)}/C_{(285 \text{ eV})}$</td>
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<td>1.41</td>
</tr>
<tr>
<td>$C_{(C=O)}/C_{(285 \text{ eV})}$</td>
<td>0.12</td>
<td>0.11</td>
</tr>
<tr>
<td>$C_{(O-C=O)}/C_{(285 \text{ eV})}$</td>
<td>------</td>
<td>0.22</td>
</tr>
<tr>
<td>$C_{(C-Mg)}/C_{(285 \text{ eV})}$</td>
<td>------</td>
<td>0.37</td>
</tr>
<tr>
<td>$C_{(285 \text{ eV})}/C_{(CFx)}$</td>
<td>0.54</td>
<td>1.25</td>
</tr>
<tr>
<td>$C_{(C-O)}/C_{(CFx)}$</td>
<td>0.12</td>
<td>1.76</td>
</tr>
<tr>
<td>$C_{(C=O)}/C_{(CFx)}$</td>
<td>0.06</td>
<td>0.14</td>
</tr>
<tr>
<td>$C_{(O-C=O)}/C_{(CFx)}$</td>
<td>------</td>
<td>0.27</td>
</tr>
<tr>
<td>$C_{(C-Mg)}/C_{(CFx)}$</td>
<td>------</td>
<td>0.46</td>
</tr>
</tbody>
</table>
Figure 5.12  High resolution spectra measured from Nafion + Ru$^{2+}$ complex thin film on PPV:

(a) C 1s and (b) O 1s.
The O 1s signal illustrated in Fig. 5.12 (b) includes oxygen adsorbed from air during the transportation of the sample from the chamber for metal evaporation to the XPS facility, but it also indicates the presence of a high content of oxygen and moisture in the high vacuum system. Two main components can be distinguished in the O 1s spectrum: the lower binding energy component at 531.4 eV (FWHM equal to 2.0 eV) is assigned to oxygen Mg-O bonding, while the higher binding energy component at 532.9 eV (FWHM equal to 2.1 eV) is assigned to links of the ether and hydroxide types.

Figure 5.13 shows F 1s spectra measured from samples with a thin and a thicker Mg layer. The data indicate the existence of direct interaction between the fluorocarbon part of Nafion and deposited Mg. The appearance of a lower binding energy component at 686.5 eV (FWHM equal to 2.5 eV) is assigned to the Mg-F interaction. This conclusion is consistent with the experimental observations of graphite fluoride film interactions with various metals published by Cadman and Gossedge [102]. The intensity ratio $F_{(\text{F-Mg})} / F_{(\text{CFx})}$ equals 0.35 for the thin Mg layer and 0.38 for the thicker deposit.

Mg 2p spectra measured from samples with the two thicknesses of deposited Mg are illustrated in Fig. 5.14. The metallic and oxide components overlap to some degree with their peaks located at 49.3 eV and 50.4 eV for the thin film and 49.1 eV and 50.2 eV for the thicker film. The ratio of the component areas oxide to metallic is 1.35 for the thin Mg film and 1.25 for the thicker film. This is taken to indicate the presence of more metallic Mg component in the thicker film. The interaction of Mg with F is not observed in the Mg 2p signal, presumably because its contribution overlaps with the oxide component.

Figure 5.15 illustrates the plasmon excitations, which are seen as small peaks on the higher binding energy side of Mg 2s and Mg 2p signals in a survey spectra, measured from samples with two different thicknesses of Mg film. These excitations result from the interaction
Figure 5.13  Comparison of F 1s spectra measured from Nafion + Ru\(^{2+}\) complex on PPV after Mg deposition: (a) thin Mg layer and (b) thicker Mg layer.
Figure 5.14 Mg 2p spectra measured from Nafion + Ru$^{2+}$ complex/PPV sample after Mg deposition: (a) thin Mg film and (b) thicker Mg film.
Figure 5.15  Plasmon excitations measured in low resolution spectra from Mg/Nafion + Ru$^{2+}$ complex/PPV samples: (a) thin Mg film and (b) thicker Mg film.
between photoelectrons and the collective oscillations of a "sea" of valence electrons [73], and their observation supports the existence of a metallic Mg component in an extensive rather than cluster form.

5.6 Electroluminescence Testing of the Mg/Nafion + Ru(bpy)$_3^{2+}$/PPV/ITO Diode

Many attempts were made to produce electroluminescence from diodes produced in this work. This section reports observations for one Mg/Nafion + Ru(bpy)$_3^{2+}$/PPV/ITO diode. These tests were done in a nitrogen box in order to reduce the influence of oxygen and moisture from air. Current could be applied to the diode through the range from 0.3 mA to 70 mA. In the example reported, yellowish light started to be emitted in spark form as the current increased from 0.3 mA to 5.7 mA, and an even more intense shining came after increasing the current from 23 mA to 57 mA. At 63 mA, a uniform shiny red light came out of the area of the diode and the light lasted for 10 sec. After the current was increased more, no further emission of red light could be recorded.

Figure 5.16 illustrates the I-V characteristic curve measured for the same Mg/Nafion +Ru(bpy)$_3^{2+}$/PPV/ITO diode. A constant current was applied at different values, and for each one the resulting voltage difference across the diode was measured. The observed shape of the I-V curve is consistent with diode behavior [103].
Figure 5.16  I-V characteristic curve measured for a Mg/Nafion + Ru(bpy)$_3^{2+}$/PPV/ITO diode.
Chapter 6  Concluding Remarks and Future Work

6.1  Summary of Results

The research discussed in this thesis gives new information for studies of interfaces in polymer light emitting devices prepared under high vacuum conditions. Two main directions have been investigated: (i) studies of PPV polymer synthesized from both undialyzed and dialyzed sulfonium precursor polymer, and changes observed in such surfaces upon Mg evaporation; (ii) fabrication of a new two-layer diode composed of PPV on ITO and Nafion with incorporated Ru(bpy)$_3^{2+}$ complex placed between the PPV and a Mg electrode. The emphasis in (ii) has been to study the interfaces in such a diode, including the changes that occur upon metal deposition.

If the sulfonium precursor of the PPV polymer is not dialyzed, the PPV formed after its thermal conversion is contaminated with oxygen impurities (at about the 10% level according to XPS) as well as lower levels of Na, Cl and Si. Studies of the C 1s high resolution spectrum indicate that the oxygen impurities are mainly in the form of C-O species, which can arise from the presence of short oxidized polymer chains with low molecular mass. Use of the Mg evaporation source under high vacuum conditions was shown to produce a substantial amount of surface oxidation; this was indicated by the observed changes in C 1s and O 1s spectra. The XPS studies of PPV, formed by thermal conversion of the dialyzed sulfonium precursor, indicated that purer polymer was synthesized compared with when an undialyzed precursor was used. It was also demonstrated that the Mg-polymer interface, obtained by metal deposition under high vacuum conditions, strongly depends on the way the PPV is prepared. The oxidation of the polymer/metal interface depends also on the evaporation rate. Mg 2p spectra show two overlapping components originating from contributions by oxide and metallic forms. But the
ratio of oxide to metallic contributions is greater when the PPV substrate is synthesized from the undialyzed precursor. To limit the deposition of unwanted oxide, lower pressures and possibly higher deposition rates are needed. The details this work are in Chapter 4, but the key point for emphasis is that interfacial properties can depend markedly on the preparation procedures used.

The results obtained with XPS from studies of Nafion and its interaction with Ru$^{2+}$ complex provided information that the Nafion surface reorients itself on exposure to aqueous solution of the Ru$^{2+}$ complex. This is believed to be driven by electrostatic interactions between incorporated Ru$^{2+}$ complex ion and SO$_3^-$ and SO$_4^{2-}$ groups. This conclusion was supported by simultaneous changes observed in O 1s and S 2p spectra. It was also found that the degree of surface rearranging depends on the thickness of the Nafion + Ru(bpy)$_3$$^{2+}$ film, which was concluded after studies of a thick film formed directly on ITO and a thin film on PPV. The thinner layer of Nafion + Ru$^{2+}$ complex on PPV undergoes a high level of surface oxidation when the Mg evaporation source is used under high vacuum. There is also evidence for direct interaction between Mg and the fluorocarbon part of Nafion; a new component is seen in the F 1s spectrum while the fluorocarbon contribution to the C 1s spectrum shows a shift in binding energy. The ratio of the oxide and metallic components in the Mg 2p spectrum was found to be dependent on the thickness of the evaporated Mg film. The thicker film has a higher metallic contribution. The binding energy position for the metallic component, and the presence of plasmon excitations, supports the conclusion that the metallic growth involves an extensive rather than cluster form. The details of these results are given in Chapter 5.

The light emission reported for the fabricated Mg/Nafion + Ru(bpy)$_3$$^{2+}$/PPV/ITO diode can only represent a starting point for these studies. It is expected that an improved understanding for the diode layer and interfacial structures can lead to improved diode performance.
6.2 Future Work

Recent developments in polymer light emitting diodes are opening a new era in fabrication of organic thin film devices. For future progress, a better understanding is needed on how to synthesize polymer chains with lower levels of defects, so that better charge transfer can occur. This statement is especially true at interfaces with electrodes. Although many studies have been made for the metal-polymer interface, particularly by depositing metal onto polymer, no similar effort has yet been made to study the polymer-ITO interface or polymer interfaces with flexible conductive substrates. The latter would provide an interesting direction for future work, especially considering the fact that little is known about the possibilities for diffusion of oxygen from ITO to polymer during the diode operation. Such investigations would be performed under UHV conditions to minimize contamination problems that may occur when working under lower-level vacuum conditions (as would be required in an industrial fabrication process).

For the new Mg/Nafion + Ru(bpy)$_3^{2+}$/PPV/ITO diode, more detailed studies are needed to understand the chemical changes occurring at interfaces, especially when the level of contamination is significantly reduced by preparing under UHV conditions. Careful control of layer thickness (especially for the Nafion layer) appears important. Exploring the effect of depositing different metals, such as Al and Ca, on to the Nafion + Ru$^{2+}$ complex, would be one direction for future work. Results for the diode prepared in this work provide a starting point for more detailed investigations of the possible voltage control for color emission. In order to understand the effect of the Nafion + Ru(bpy)$_3^{2+}$ layer on electron injection from the metal electrode, measurements of current density and light emission vs. voltage over extended period of time must be made. Also, it would be very interesting to study the influence of other
luminescent compounds (for example involving Ru and Os complexes) which could be ionically exchanged in Nafion.
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