# AD-A234 598 DOCUMENTATION PAGE

| 1a. REPORT<br>Unclassified | 1b. RESTRICTIVE MARKINGS DTIC |
|---|---|
| 2a. SECURITY CLASSIFICATION AUTHORITY | 3. DISTRIBUTION / AVAILABILITY OF REPORT ELECT<br>APR 22 1991 |
| 2b. DECLASSIFICATION / DOWNGRADING SCHEDULE | |
| 4. PERFORMING ORGANIZATION REPORT NUMBER(S)<br>Technical Report No. 26 | 5. MONITORING ORGANIZATION REPORT NUMBER(S) C |

| 6a. NAME OF PERFORMING ORGANIZATION<br>The University of Texas at Arlington | 6b. OFFICE SYMBOL<br>(If applicable) | 7a. NAME OF MONITORING ORGANIZATION<br>Office of Naval Research |
|---|---|---|
| 6c. ADDRESS (City, State, and ZIP Code)<br>Center for Advanced Polymer Research<br>Department of Chemistry, Box 19065, University<br>of Texas at Arlington. Arlington, TX. 76019 | | 7b. ADDRESS (City, State, and ZIP Code)<br>800 North Quincy Street<br>Arlington, Virginia 22217 |
| 8a. NAME OF FUNDING / SPONSORING<br>ORGANIZATION Defense Advanced<br>Research Projects Agency | 8b. OFFICE SYMBOL<br>(If applicable)<br>DARPA | 9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER<br>N00014-90-J-1320 |

| 8c. ADDRESS (City, State, and ZIP Code)<br>1410 Wilson Boulevard<br>Arlington, Virginia 22209 | 10. SOURCE OF FUNDING NUMBERS | | | |
|---|---|---|---|---|
| | PROGRAM<br>ELEMENT NO. | PROJECT<br>NO. | TASK<br>NO. | WORK UNIT<br>ACCESSION NO. |

**11. TITLE (Include Security Classification)**
Surface Characterization of Electrically Conducting Nickel Tetrathiooxalate/Poly(vinyl alcohol) Composites

**12. PERSONAL AUTHOR(S)**
W. F. Stickle, J. R. Reynolds and C. A. Jolly

| 13a. TYPE OF REPORT<br>Technical | 13b. TIME COVERED<br>FROM_____ TO_____ | 14. DATE OF REPORT (Year, Month, Day)<br>April 12, 1991 | 15. PAGE COUNT<br>16 |
|---|---|---|---|

**16. SUPPLEMENTARY NOTATION**
Paper in press in Langmuir

| 17. | COSATI CODES | | 18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) |
|---|---|---|---|
| FIELD | GROUP | SUB-GROUP | Nickel tetrathiooxalate; poly(vinyl alcohol); composites; XPS; SSIMS |

**19. ABSTRACT (Continue on reverse if necessary and identify by block number)**

Nickel(II) acetate, complexed in poly(vinyl alcohol) (Ni/PVA) has been reacted with tetraethylammonium tetrathiooxalate (TEATTO) to form a semiconductive composite (NiTTO/PVA). The resulting materials are air stable and mechanically durable with conductivities up to $10^{-3}\ \Omega^{-1}\ cm^{-1}$. Examination of the surfaces by X-ray photoelectron spectroscopy (XPS) prior to treatment with TEATTO indicates the Ni/PVA surface to contain Ni(II) in an octahedral coordination. After reaction with TEATTO to form NiTTO/PVA the Ni(II) is observed to be in a square planar coordination. The chemistry and composition of the Ni/PVA precursors, their TEATTO reaction products and model compounds, as characterized by XPS and static secondary ion mass spectrometry (SSIMS), are compared and contrasted.

| 20. DISTRIBUTION / AVAILABILITY OF ABSTRACT<br>☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS | 21. ABSTRACT SECURITY CLASSIFICATION<br>Unclassified | |
|---|---|---|
| 22a. NAME OF RESPONSIBLE INDIVIDUAL<br>Dr. JoAnn Milliken | 22b. TELEPHONE (Include Area Code)<br>(202) 696-4410 | 22c. OFFICE SYMBOL |

91 4 19 027

DEFENSE ADVANCED RESEARCH PROJECTS AGENCY/OFFICE OF NAVAL RESEARCH

# Surface Characterization of Electrically Conducting Nickel Tetrathiooxalate/ Poly(vinyl alcohol) Composites

by

W. F. Stickle

J. R. Reynolds

C. A. Jolly

Center for Advanced Polymer Research
Department of Chemistry
Box 19065
The University of Texas at Arlington
Arlington, Texas 76019-0065

April 12, 1991

A-1

# Surface Characterization of Electrically Conducting Nickel Tetrathiooxalate/Poly(Vinyl Alcohol) Composites

W.F. Stickle, Perkin-Elmer Physical Electronics Laboratories, 6509 Flying Cloud Drive, Eden Prairie, MN 55344

J. R. Reynolds and C. A. Jolly, Center for Advanced Polymer Research, Department of Chemistry, The University of Texas at Arlington, Arlington, TX 76019-0065

## Abstract

Nickel(II) acetate, complexed in poly(vinyl alcohol) (Ni/PVA) has been reacted with tetraethlyammonium tetrathiooxalate (TEATTO) to form a semiconductive composite (NiTTO/PVA). The resulting materials are air stable and mechanically durable with conductivities up to $10^{-3}$ $\Omega^{-1}$ cm$^{-1}$. Examination of the surfaces by X-ray photoelectron spectroscopy (XPS) prior to treatment with TEATTO indicates the Ni/PVA surface to contain Ni(II) in an octahedral coordination. After reaction with TEATTO to form NiTTO/PVA the Ni(II) is observed to be in a square planar coordination. The chemistry and composition of the Ni/PVA precursors, their TEATTO reaction products and model compounds, as characterized by XPS and static secondary ion mass spectrometry (SSIMS), are compared and contrasted.

## Introduction

Electrically conductive polymers are presently used, and have been considered for use, in applications that include battery electrodes, EMI shielding and static discharge. A significant amount of work has been directed to the preparation of conducting organic polymers with carriers introduced onto extended conjugated polymer chains via redox doping.[1] A second method used to prepare conducting polymers has involved the complexation of transition metal ions by conjugated bridging ligands. This is exemplified by the synthesis of poly(metal tetrathiooxalates),[2-4] poly(metal ethylenetetrathiolates),[5-7] poly(metal tetrathiosquarates),[8] poly(metal tetrathiafulvalenetetrathiolates),[9-10] poly(metal tetrathianaphthalenes)[11] and poly(metal benzenetetrathiolates).[12] In general, these polymers are insoluble and infusible and, while displaying useful electronic conductivity and ambient stability, they are not processable to form a mechanically durable material.

Recently, we have extended a method of preparing metal complex polymers within polar matrix polymers[13] to form semiconductive composites which retain the mechanical properties of the host polymer.[14,15] In addition to their charge-transport characteristics, these composites can be stretch oriented to yield optically polarizing films. The synthetic method employed involves first forming a homogeneous complex of the matrix polymer [poly(vinyl alcohol) (PVA)] and the metal ion [Ni(II)] as a free-standing film (Ni/PVA). Subsequent diffusion of reactive tetrathiooxalate ligand into this membrane leads to poly(nickel tetrathiooxalate) chains forming within the PVA matrix as a composite (NiTTO/PVA) as outlined in scheme I. The reaction of the TEATTO with Ni(II) begins at the membrane/solution interface and proceeds as the ligand penetrates into the bulk of the film. Since this reaction occurs initially on the film surface, coupled with the fact that many applications are surface sensitive, we have undertaken an analysis of the surface structure of the NiTTO/PVA using X-ray photoelectron spectroscopy (XPS) and static secondary ion mass spectrometry (SSIMS) and report our results here. These results are compared to Ni/PVA, prior to complexation, polymeization and model compounds.

## Experimental

Ni/PVA and NiTTO/PVA films of 100 μm thickness were prepared as reported previously.[14,15] For this study, films having an initial Ni/PVA repeat unit ratio of 1/11 were employed. As the complexation reaction is heterogeneous and partially confined to the membrane surface, determination of Ni/TTO ratios was not possible. Where noted, samples were polished with tissue paper to remove powdery deposits of NiTTO. Ni(dmit)$_2$, structure 1, [dmit = Bis(1,3-dithiole-2-thione-4,5-dithiolato)] was prepared as described previously[16-18] as a representative square-planar complex containing the NiS$_4$ center.

The analysis of the surface of organic materials may be accomplished by several methods, which includes XPS, also known as Electron Spectroscopy for Chemical Analysis (ESCA) and SSIMS. XPS and SSIMS are complementary techniques which provide both short range chemical bonding information (XPS), and long range chemical structural information (SSIMS) which is important in the analysis of organic materials. Each of these surface sensitive analytical techniques reveal unique information which, together, provide a complete picture of the surface. XPS and SSIMS data were acquired for Ni(II)/PVA, tetraethylammonium tetrathiooxalate (TEATTO) and the NiTTO/PVA

composites. The XPS data were acquired with a Perkin-Elmer model 5400 ESCA system using monochromatic Al radiation. The data were acquired from an 800μm diameter area and referenced to the carbon 1s at 284.8 eV. The SSIMS data were acquired with a Perkin-Elmer model 3700 SIMS unit using Xe+ ions. The sampling depth of the XPS experiments is about 70Å while the sampling depth of the SSIMS experiments is less than 5Å.

## Discussion

In order to determine the surface structure of the NiTTO/PVA composites, the Ni(II)/PVA and TEATTO reactants were first analyzed. A solution cast Ni(II)/PVA film is light green and transparent due to the complexation of the Ni(II) by the polymer. The C 1s spectrum of this film, Figure 1, shows the hydrocarbon peak at 284.8 eV (figure 1a) and some reduction in the expected intensity of the COH peak (figure 1b) when it has solubilized the Ni (II),[19] however this spectrum is not characteristic of the pure 100% hydrolyzed PVA as noted by the presence of the O=C-O functional group at about 289 eV (figure 1c). This is expected since the polymer bound PVA-OH functional groups do not displace the charge balancing acetate anions, but only to serve to coordinate with the nickel ion. The positive SSIMS is characteristic of a hydrocarbon polymer with the main peak being the PVA monomer, $C_2H_4O^+$, less a hydrogen at 43 dalton.

The tetraethylammonium tetrathiooxalate ligand has a S 2p spectrum which is typical for this class of organic ligand,[20,21] Figure 2, where the spin-orbit splitting of the S 2p is clearly observed in peak a. One chemical environment is observed for the four equivalent sulfur atoms in the $C_2S_4$ dianion at a binding energy of about 163 eV which is consistent with organic carbon - sulfur bonds. Some oxidation of the surface of the crystalline material is also observed (peak b) as sulfate at a binding energy of about 168.5 eV. The positive SSIMS analysis shows a characteristic peak at 130 dalton of the tetraethylammonium counter ion, while the negative SSIMS analysis shows fragmentation of $C_2S_4^{2-}$ with $S^-$, $C_2S_2^-$ and $C_2S_3^-$ fragments at 32, 88, and 120 dalton respectively.

The reaction of the Ni(II)/PVA with $C_2S_4^{2-}$ is expected to lead to the formation of square planar $NiS_4$ centers with the $C_2S_4^{2-}$ acting as bridging ligands between metal ions along a chain. The XPS data of a model compound, Ni(dmit)$_2$, which has a square planar

structure are shown in Figures 3a and 3b. The Ni 2p spectrum in Figure 3a is characteristic of Ni(II) in a square planar coordination as noted by the lack of shake-up satellite structure[22] which would appear on the high binding energy side of the Ni 2p peaks. The S 2p spectrum in Figure 3b shows two distinct sulfur environments of C-S bonds and nickel-S bonds. A small amount of sulfate is also observed at about 168.5 eV.

The reaction of the Ni(II)/PVA membrane with a methanolic solution of the $C_2S_4^{2-}$ ligand produces a square planar nickel (II) complex on the surface which is conductive. It should be noted that the complex is incorporated into the PVA, and is not just a surface coating, as the material retains its conductivity after surface polishing to remove any powdery NiTTO not bound in the PVA matrix. This nickel complex is confirmed by the XPS data for the Ni(II), Figure 4a, which shows the surface to contain both octahedral and square planar coordination nickel (II). Figure 4b illustrates the octahedrally coordinated Ni(II) of the Ni(II)/PVA reactant surface. The octahedral coordination is noted by the intense shake-up satellites which are 5 eV higher than the Ni 2p lines. Figure 4c shows the Ni 2p of the square planar $Ni(dmit)_2$ where the shake-up satellites are not observed. Most of the nickel in the composite matrix is observed to be in a square planar coordination, indicating significant formation of the NiTTO complex, although not all of the nickel has reacted, as suggested by the small amount of octahedrally coordinated Ni(II) still observed in the sample surface. These results are in agreement with large angle x-ray scattering results of NiTTO which originally suggested square planar coordination for these complex polymers.[4] This is the first such measurement on these composites and indicates that the $C_2S_4^{2-}$ is effectively removing the Ni(II) from the PVA chains. Though the NiTTO is forming within the PVA matrix, under the conditions used here of 30 minutes reaction with ligand at room temperature, complexation does not occur throughout the film bulk. This heterogeneity due to incomplete reaction may explain the octahedrally coordinated nickel still detected in the NiTTO/PVA composite. This will be detailed in further work.

The S 2p data, Figure 5, reveals sulfur in two chemical environments instead of the single Ni-S-C environment which would be expected from an infinite chain of NiTTO. The binding energies of the C-S and Ni-S environments observed in the composite are consistent with the Ni(dmit)2 data. The fact that two S 2p chemical environments are observed in these composites suggests that the NiTTO chains are quite short and are terminated by the $C_2S_4^{2-}$ ligands. Thus the second C-S sulfur environment represents end groups. The C 1s data are also characteristic of PVA.

The SSIMS data analysis of the surface after reaction shows the tetraethylammonium counterion for the complex to be present on the surface as evidenced by the appearance of the 130 dalton peak in the positive SSIMS analysis. This is expected with the charged $C_2S_4$ end groups. Though residual tetraethylammonium acetate on the film surface would give similar results, the samples were soaked and thoroughly rinsed prior to analysis and, thus this is not expected. However, the negative SSIMS analysis does not show the fragmentation pattern of the tetrathiooxalate as the 88 and 120 dalton peaks are missing although S⁻ at 32 dalton is observed.

## Conclusions

The Ni/PVA films prior to complexation with tetrathiooxalate exhibit no change in electrical properties with conductivities $<10^{-7} - 10^{-8}$ $\Omega^{-1}$ cm$^{-1}$. The XPS data also suggest that the nickel is complexed within the PVA matrix as observed in the change of the C-OH intensity. After reaction with the TEATTO electrical conductivity is elevated to $10^{-3}$ $\Omega^{-1}$ cm$^{-1}$. The reaction with the TEATTO occurs at the surface. The XPS data clearly show the formation of a square planar nickel (II) complex as NiTTO chains form within the PVA matrix as a composite.

## Acknowledgements

## References

1. Skotheim, T. A. (ed.); "Handbook of Conducting Polymers", Marcel Dekker, New York, 1986
2. Reynolds, J. R.; Karasz, F. E.; Lillya, C. P.; Chien, J.C.W. *J. Chem. Soc., Chem. Commun.*, **1985**, 268.
3. Reynolds, J. R. ; Chien, J.C.W. ; Lillya, C.P. *Macromolecules*, **1987**, *20*, 1184.
4. Reynolds, J. R.; Jolly, C. A.; Krichene, S.; Cassoux, P.; Faulmann, C. *Synth. Met.*, **1989**, *31*, 109.
5. Engler, E. M.; Nichols, K. H.; Patel, V. V.; Rivera, N. M.; Schumaker, R. R. U.S. Patent 4,111,857; 1978.

6.  Poleschner, H.; John, W.; Hoppe, F.; Fanghanel, E. *J. Prakt. Chem.*, 1983, *325*, 957.
7.  Vicente, R.; Ribas, J.; Cassoux, P.; Valade, L. *Synth. Met.*, 1986, *13*, 265.
8.  Gotzfried, F.; Beck, W.; Lerf, A.; Sebald, A. *Angew. Chem., Int. Ed. Engl.*, 1979, *18*, 463.
9.  Rivera, N. M.; Engler, E. M.; Schumaker, R. R.; *J. Chem. Soc., Chem. Commun.*, 1979, 164.
10. Ribas, J.; Cassoux, P. C. *R. Acad. Sci., Ser. B*, 1981, *293*, 665.
11. Teo, B. K.; Wudl, F.; Hauser, J. J.; Kruger, A. *J. Am. Chem. Soc.*, 1977, *99*, 4862.
12. Dirk, C. W.; Bousseau, M.; Barrett, P. H.; Moraes, F.; Wudl, F.; Heeger, A. J. *Macromolecules*, 1986, *19*, 266.
13. Amon, W. F.; Kane, M. W. U. S. Patent 2 505 085, 1950
14. Jolly, C. A.; Ph.D. Dissertation, The University of Texas at Arlington, 1989
15. Jolly, C. A.; Reynolds, J. R. *Chem. Mater.*, 1990, 2, 479
16. Steimeke, G.; Sieler, H. J.; Kirmse, R.; Hoyer, R. *Phosphorous and Sulfur*, 1979, 7, 49.
17. Ribas, J.; Cassoux, P. C. *R. Acad. Sci., Ser. B*, 1981, *293*, 287.
18. Valade, L.; Bousseau, M.; Gleizes, A.; Cassoux, P. *J. Chem. Soc., Chem. Comm.*, 1983, 110
19. Burkstrand, J. M. *J. Vac. Sci. Technol.*, 1979, *16*, 363
20. Wagner, C. D.; Taylor, J. A. *J. Elecir. Spec. Relat. Phenom.*, 1982, 28, 211
21. Lindberg, B. J.; Hamrin, K.; Johansson, G.; Gelius, U.; Fahlman, A.; Nordling, C.; Siegbahn, K. *Phys. Scr.*, 1970, *1*, 286
22. Matienzo, L. J.; Yin, L. I.; Grim, S. A.; Swartz, W. E. *Inorg. Chem.*, 1973, *12*, 2762.
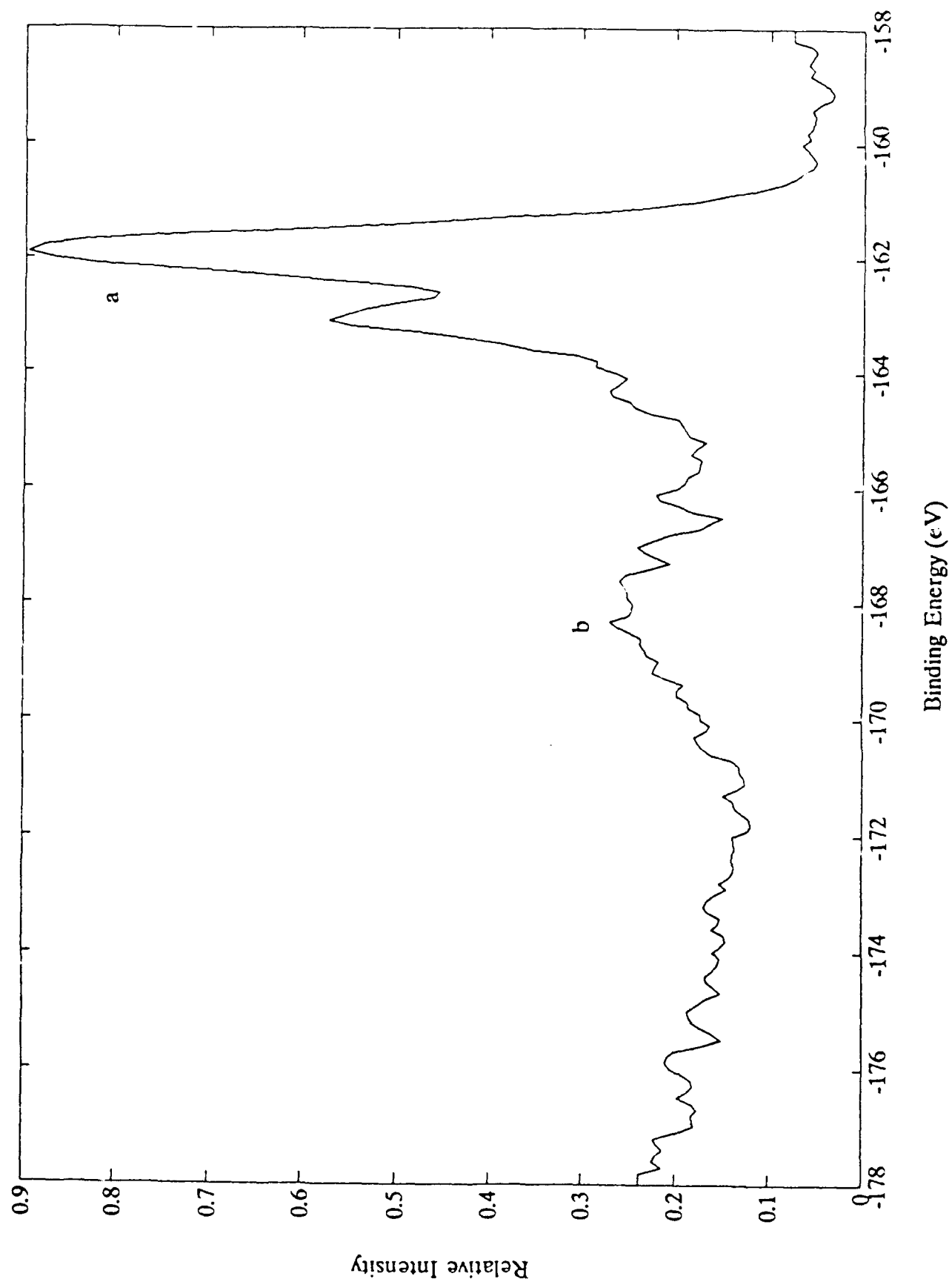
**Figures**

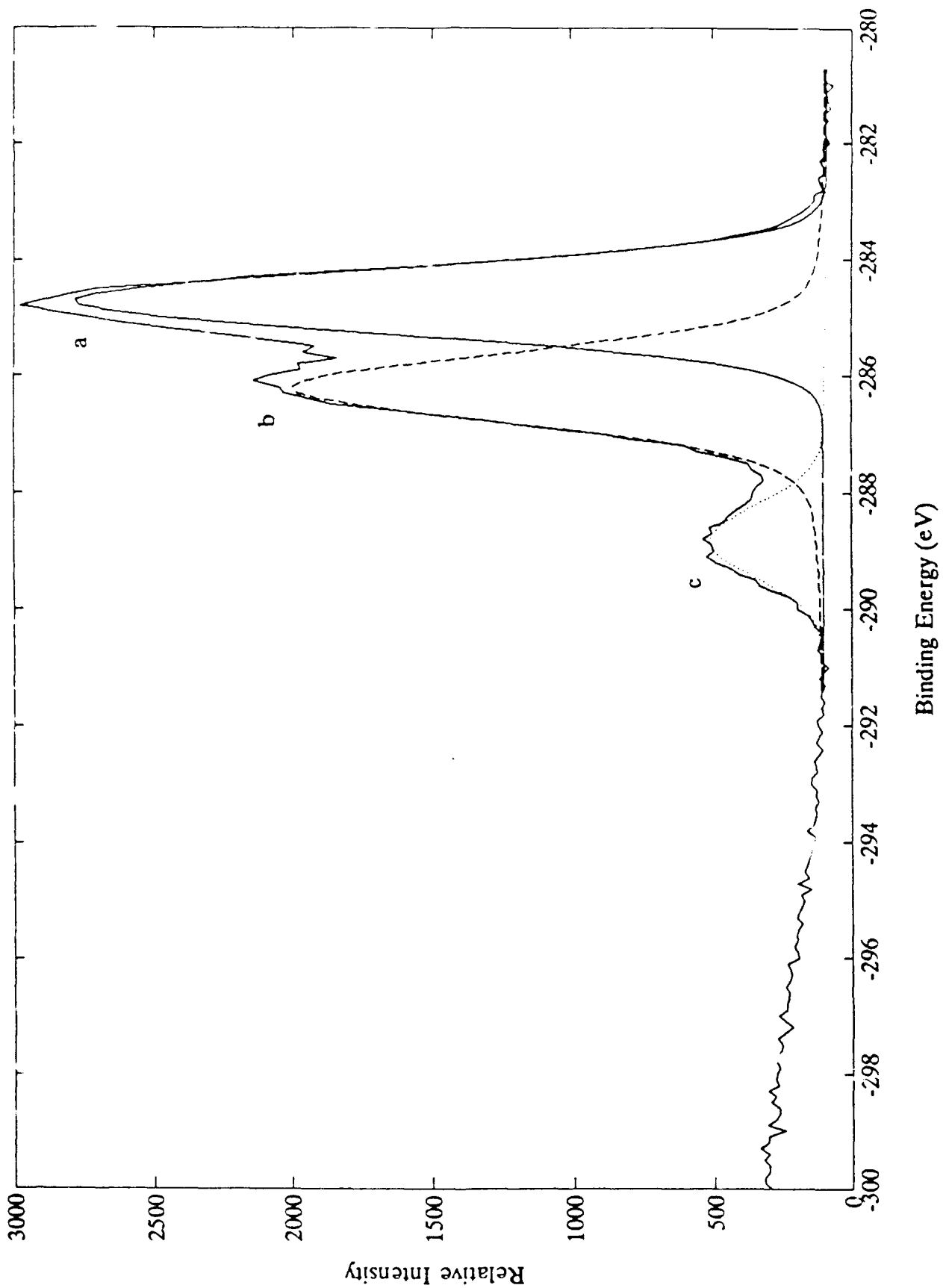Figure 1. XPS spectrum of the C 1s of Ni(II)/PVA film.

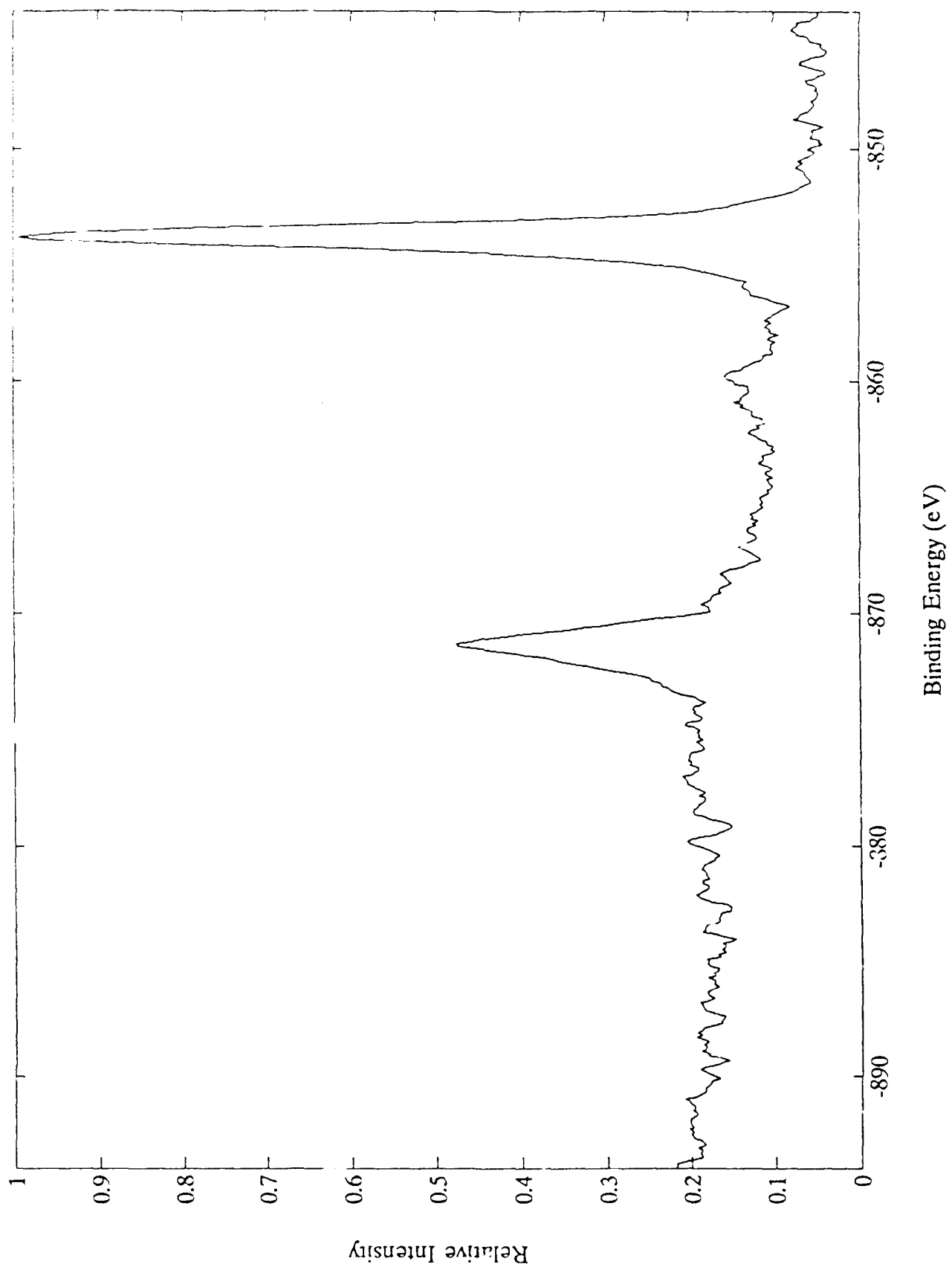Figure 2. XPS spectrum of the S 2p of tetraethylammonium tetrathiooxalate.

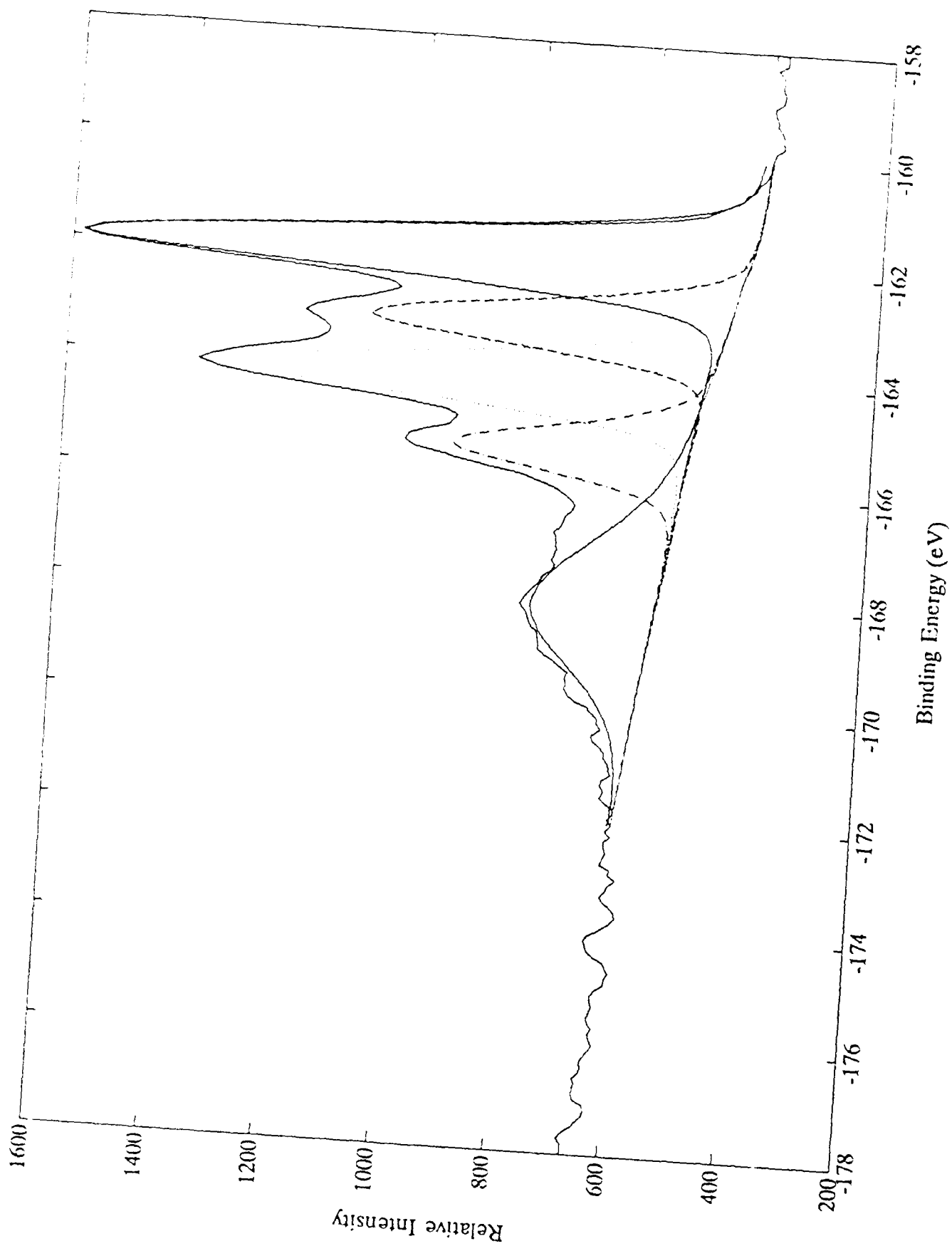Figure 3 a) XPS spectrum of the Ni 2p of Ni(dmit)$_2$. b) XPS spectrum of the S 2p of Ni(dmit)$_2$.

Figure 4. a) XPS spectrum of the Ni 2p of the NiTTO in the composite matrix. b) XPS spectrum of the octahedrally coordinated Ni(II) of the Ni(II)/PVA surface. c) XPS spectrum of the Ni 2p of square planar Ni(dmit)$_2$.
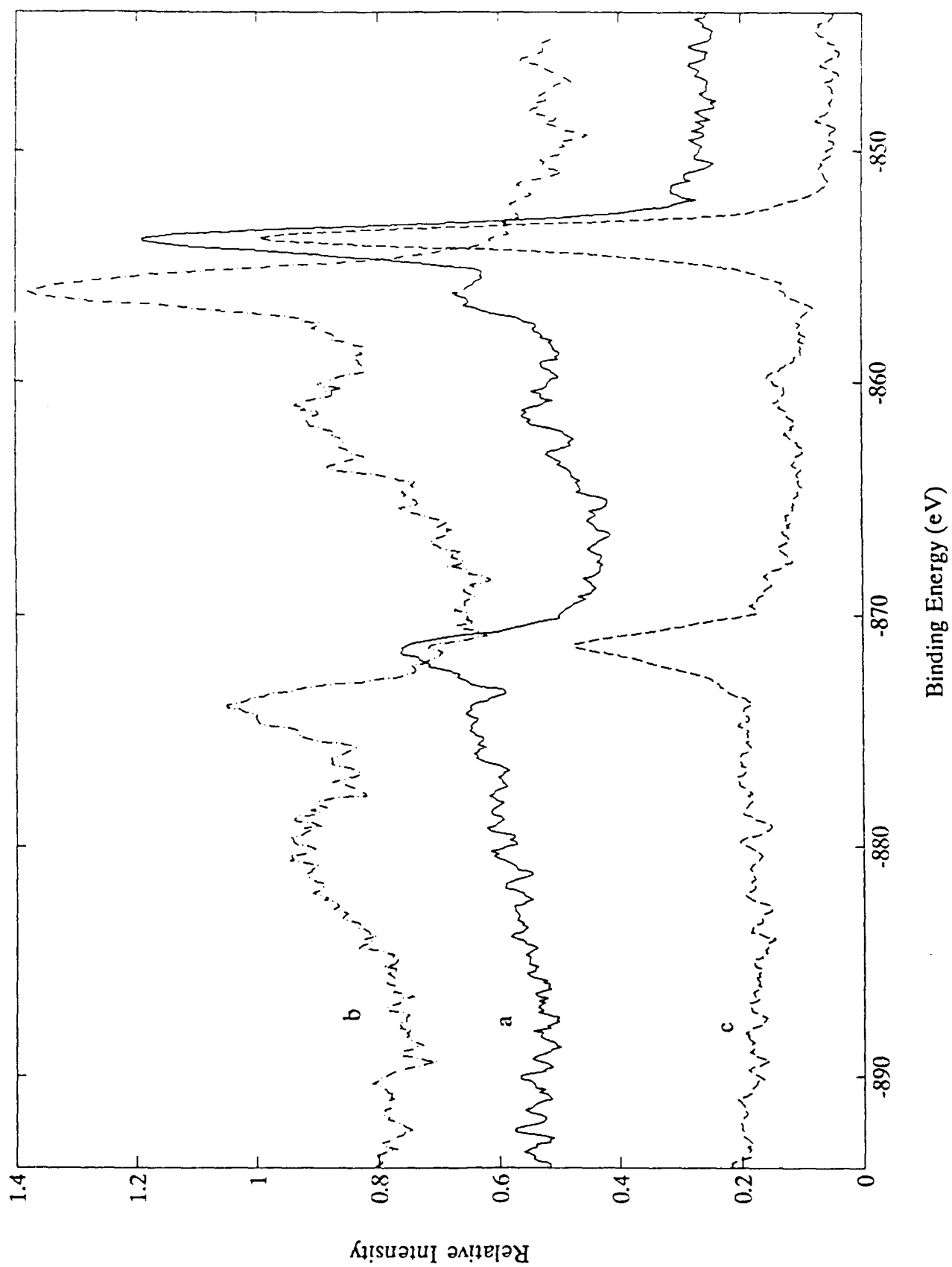
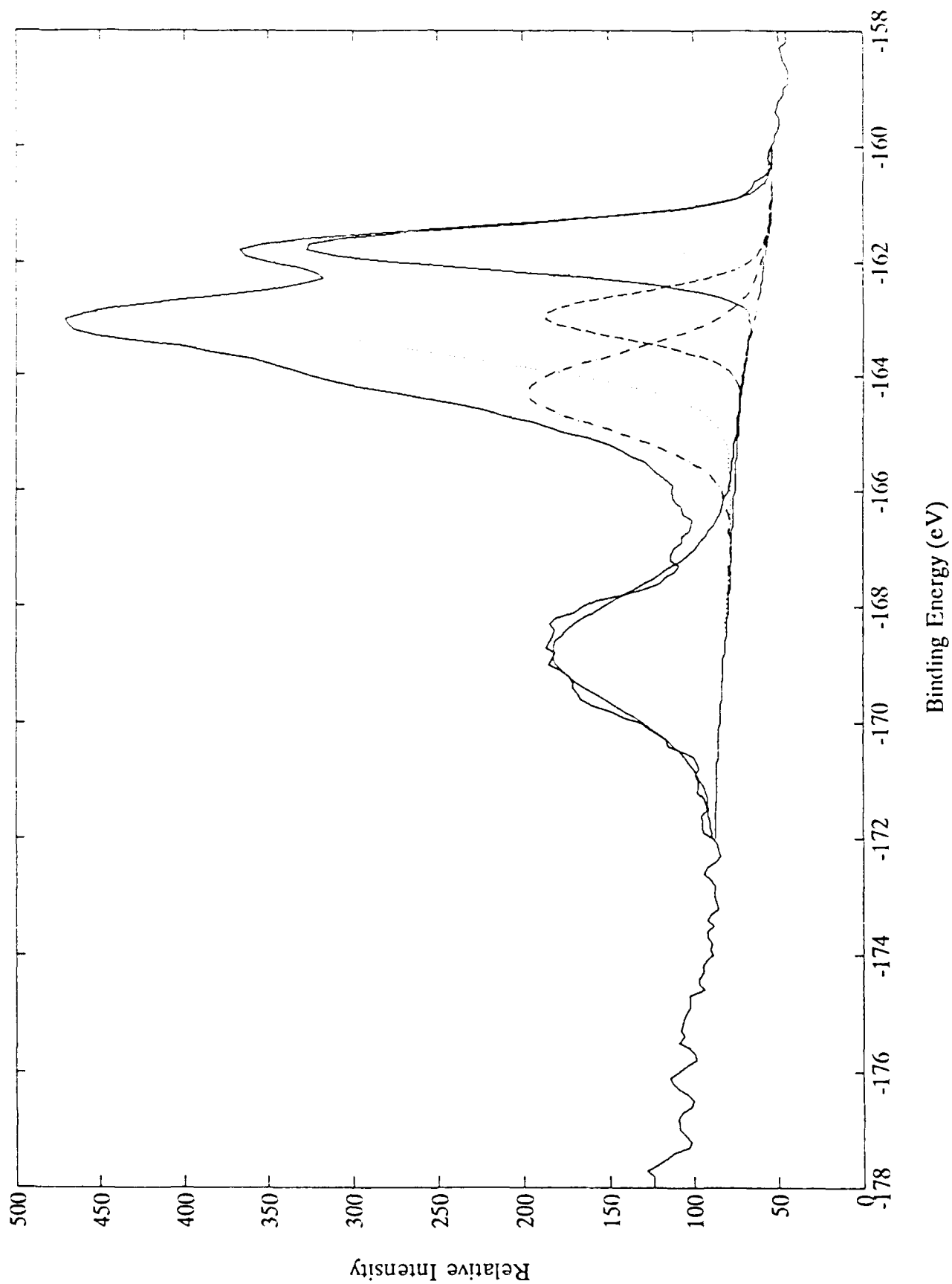Figure 5. XPS spectrum of the S 2p of the NiTTO in the composite matrix
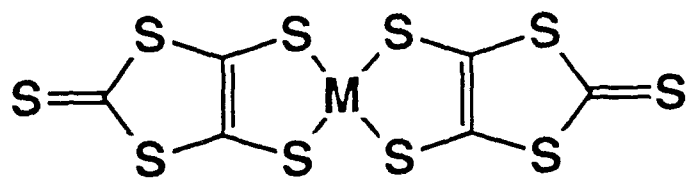
Relative Intensity

Binding Energy (eV)

Relative Intensity

Binding Energy (eV)

Binding Energy (eV)

Relative Intensity

Binding Energy (eV)

Relative Intensity

Relative Intensity

Binding Energy (eV)

1

Scheme I



Ni(OAc)$_2$·(4H$_2$O)

Ni/PVA

(Et$_4$N)$_2$C$_2$S$_4$

+ 2 Et$_4$NOAc

NiTTO/PVA