XPS STUDY OF Ni-Fe MANGANITE THERMISTOR MATERIAL

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ABSTRACT

The resistivity of the as-fabricated thermistor material, nickel-iron-manganite, changes during initial aging in the temperature range of 150-300°C before becoming stable. X-ray photoelectron spectroscopy (XPS) was used to determine if any valency change or chemical shift of the cations or oxygen occurred after aging. The goal of the study was to identify any ionic changes that might affect thermistor stability. The only observed changes in $2p_{3/2}$ peaks due to aging were those related to Ni ions; the same peaks for Mn, Fe, and O remained unchanged. The changes in the Ni $2p_{3/2}$ peak may be related to: (a) the migration of Ni^{2+} ions from octahedral to tetrahedral sites, (b) subtle changes in the energy states of Ni^{2+} which promoted a more stable ionic structure, and/or (c) the presence of Ni^{3+} ions, some of which revert back to Ni^{2+} .

INTRODUCTION

Nickel-iron-magnetite, $Ni_{1-x}(MnFe)_{2+x}O_4$, is a semiconducting oxide exhibiting a negative temperature coefficient of resistance (NTC) that is widely used in a number of applications to sense temperature. Theoretically, this thermistor material should have an inverse spinel structure (cubic) with the A^{2+} ions and half the B^{3+} ions on octahedral sites, and the other half of the B^{3+} on tetrahedral sites, or $B(AB)O_4$.¹ In actuality, the cation valency distribution which controls the electrical properties of the material is not well understood. Previous investigators have used x-ray photoelectron spectroscopy (XPS),²⁻⁵ magnetic or electrical measurements,⁶⁻⁸ and other techniques to study the cation valencies in similar oxides. Unfortunately, the conclusions drawn from the different studies have often been in disagreement.

In this study, the effect of thermal aging on the ionic structure of the thermistor material was analyzed using XPS. Any possible change in structure that developed after fabrication during the initial aging at 150-300°C was of specific interest because of the relatively large resistivity changes previously observed. Standard 100 k Ω thermistors were analyzed before and after aging with particular attention paid to binding energy measurements of the cations at the $2p$ levels. The goal of the study was to identify any ionic changes that might affect the stability of the thermistor's resistivity.

EXPERIMENTAL

Small, 2.3 mm diam. x 0.43 mm thick thermistor disks were taken from the production stock of 100 k Ω devices for analysis. The disks were fabricated by blending powders of NiO , Mn_2O_3 , and Fe_2O_3 , adding binder, ball-milling, pressing into disks, and finally firing in air at 1300°C. The composition contained about 20 wt.% Ni, with the balance about evenly distributed between Mn and Fe. The disks were analyzed in the as-fabricated as well as the thermally-aged conditions. Aging was conducted in an electrical-resistance furnace, in air, at 300°C for 3 and 9 days. Furnace temperature was controlled within $\pm 1^\circ C$.

The thermistor disks were analyzed in a PHI Electronics 5600 x-ray photoelectron spectrometer, using monochromated $Al_{K\alpha}$ x-rays at 15 kV and 400 watts with a 0.4 mm diam. aperture. A low-energy electron flood gun was employed to minimize specimen charging. Samples of the starting NiO , Mn_2O_3 , and Fe_2O_3 powders, used to fabricate the thermistors, were analyzed under identical operating conditions and used as standards. Examination of these oxide powders by

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x-ray diffraction verified their respective identities and showed there were no extraneous oxides or other second phases present. Pure metal standards of Ni (99.998%), Mn (99.99%), and Fe (99.999%) from Geller Microanalytical Laboratory, Peabody, MA (Standard UHV-EL) were also analyzed under the same operating conditions. Argon sputtering at 4 kV was used to remove normal surface contamination. In analyzing the XPS spectra, binding energies were referenced to 285.0 eV for the C 1s peak of hydrocarbon contamination due to air exposure (adventitious carbon). Curve-fitting of the spectra was conducted using Gaussian/Lorentzian line shapes after removal of the background.

RESULTS

Results of the XPS analyses are summarized in Fig. 1. The $2p_{3/2}$ peaks for the pure metal standards of Mn, Fe, and Ni (Fig. 1a) and starting oxide powders (Fig. 1b) are shown at the bottom of each figure. The same peaks for each respective ion in the spinel are shown for the as-fabricated thermistor material (Fig. 1c), and after aging at 300°C for three (Fig. 1d) and nine days (Fig. 1e). Binding energies (BE) for Mn, Fe, and Ni for each material and condition are listed in Table 1 under the column labeled $2p_{3/2}$. The full width half maximum (FWHM) for each peak is also listed, along with data for the satellite structure and the $2p_{3/2}$ - $2p_{1/2}$ separation. The O-1s BE of 529.6 eV did not change for any of the conditions and is not listed.

The $2p_{3/2}$ peak for Mn metal had a BE of 638.6 eV and a $2p_{3/2}$ - $2p_{1/2}$ separation of 11.1 eV (Table 1) which compares favorably with the values of 639.0 and 11.05 eV, respectively, listed in the handbook.¹ The same Mn peak in the Mn_2O_3 powder had a BE of 641.6 eV with a shake-up satellite of 645.7 eV and a $2p_{3/2}$ - $2p_{1/2}$ separation of 11.6 eV. The Mn peaks in the as-fabricated spinel were virtually identical to those in the Mn_2O_3 powder and thermal aging for 3 or 9 days showed no effect on the peaks (Fig. 1 and Table 1).

A $2p_{3/2}$ BE of 706.38 eV and a $2p_{3/2}$ - $2p_{1/2}$ separation of 13.2 eV was measured for Fe metal (Table 1) which, again, compared well with handbook values of 707.0 and 13.10 eV.⁹ The same two parameters for the Fe_2O_3 powder were 710.1 and 13.7 eV (Table 1) while handbook values were 710.9 and 13.6 eV.¹ As in the case for Mn, the $2p_{3/2}$ peak shape and BE's for Fe were the same for the starting oxide, the as-fabricated disks, and the thermally aged material (Fig. 1 and Table 1). The two shake-up satellite peaks in the left portion of the broadened $2p_{3/2}$ peak of the oxide were also found in the spinel.

The $2p_{3/2}$ peak for Ni metal had a slightly lower BE of 852.0 eV (Table 1) compared to the 852.7 eV handbook value.⁹ However, the experimental value for the $2p_{3/2}$ - $2p_{1/2}$ separation of 17.2 eV agreed closely with that in the handbook, 17.27 eV.⁹ A weak, broad peak due to plasmon losses was observed at 857.8 eV. The $2p_{3/2}$ Ni peak in the starting NiO powder has a complex structure as shown in Fig. 1. Its measured BE of 852.8 eV is 1 eV lower than the 853.8 eV handbook value,⁹ but the $2p_{3/2}$ - $2p_{1/2}$ separation of 17.3 eV agrees well with the handbook value of 17.49 eV. As shown in the handbook⁹ and others,^{5,10-12} the $2p_{3/2}$ peak exhibits multiplet splitting and a number of shake-up satellites. Although the BE of this peak remained the same in the as-fabricated and thermally-aged materials, the satellite structure was remarkably different, as shown in Fig. 1, and in more detail in Fig. 2. The $2p_{3/2}$ Ni peak in NiO exhibited three shake-up satellites while that for the as-fabricated spinel had only two. The first satellite in the as-fabricated spinel (855.2 eV) was relatively large and decreased substantially after 3 days of thermal aging at 300°C, as shown in Figs. 2. Further aging at the same temperature for 9 days had no effect on the peak shape.

DISCUSSION

Nickel was the only cation in the 100 k Ω thermistor material that exhibited changes in its $2p_{3/2}$ peak after thermal aging. The intensity of the first satellite was lowered by nearly a factor of 2 relative to the $2p_{3/2}$ after the initial aging treatment of 3 days at 300°C, and then remained constant

Fig. 1 Mn-, Fe-, and Ni- $2p_{3/2}$ and $2p_{1/2}$ XPS peaks in (a) metal, (b) oxide, (c) as-fabricated thermistor spinel, (d) spinel after 3 d at 300°C, and (e) spinel after 9 d at 300°C.

Fig. 2 Changes in Ni-2p_{3/2} satellite structure from NiO to that in as-fabricated spinel and spinel after aging for 3 days at 300°C.

TABLE 1 - XPS DATA										
ELEMENT	CONDITION	2p3/2 (eV)	FWHM (eV)	Satellite1 (eV)	FWHM (eV)	Satellite2 (eV)	FWHM (eV)	Satellite3 (eV)	FWHM (eV)	2p3/2-2p1/2 (eV)
Mn	Metal	638.6	1.3							11.1
Mn Oxide	Powder	641.6	3.1	645.7	5.8					11.6
SPINEL (Mn)	As-Fabricated	641.4	3.6	646.4	4.4					11.4
SPINEL (Mn)	3 days @ 300C	641.3	3.5	646.3	6.0					11.8
SPINEL (Mn)	9 days @ 300C	641.3	3.6	646.3	4.1					11.5
Fe	Metal	706.4	1.4							13.2
Fe Oxide	Powder	710.1	3.5	713.1	4.8	718.0	5.0			13.7
SPINEL (Fe)	As-Fabricated	709.9	4.0	713.3	4.8	717.4	4.4			13.5
SPINEL (Fe)	3 days @ 300C	710.2	4.6	713.8	4.9	717.9	5.1			13.2
SPINEL (Fe)	9 days @ 300C	709.9	4.4	713.1	5.4	717.8	6.1			13.3
Ni	Metal	852.0	1.6			857.8	5.6			17.2
NiO	Powder	852.8	1.5	854.3	2.2	856.5	3.4	861.1	5.2	17.3
SPINEL (Ni)	As-Fabricated	852.8	1.3	855.2	5.0			861.6	4.3	17.3
SPINEL (Ni)	3 days @ 300C	852.8	1.4	855.2	5.1			860.9	4.8	17.2
SPINEL (Ni)	9 days @ 300C	852.9	1.4	855.4	5.4			861.3	3.9	17.2

upon further aging. At the same time, Mn and Fe 2p peaks as well as the O 1s peak showed no evidence of chemical shifts or even changes in peak shape. It is possible that the changes in the Ni 2p_{3/2}/satellite structure were due to Ni³⁺ as reported by Hashemi and Brinkman² for a similar thermistor material which contained Cu instead of Fe. The apparent Ni³⁺ binding energy was ≈2.1 eV higher than that for Ni²⁺ which agreed with the 2.2 eV measured by Ng and Hercules⁵ for Ni in Ni-oxides. The relatively intense satellite peak observed in the present work is located somewhat further away (≈2.5 eV) but still might be interpreted as Ni³⁺. If Ni³⁺ was present after fabrication, then a portion of it would have to revert back to Ni²⁺ upon aging to account for the reduction of intensity shown in Fig. 2. However, it is difficult to prove that Ni³⁺ is present and not just a complex satellite structure similar to the one found in NiO (Fig. 2). Moreover, the presence of the Ni³⁺ ion in the nickel iron manganite would be considered somewhat unusual because most investigators^{4,7,13-15} list only Ni²⁺ in their cation distributions in nickel manganite.

The observed changes in the Ni 2p_{3/2} peaks could be due to changes in the shake-up satellite structure itself. Vernon et al¹⁶ point out that intense satellites are often observed in Ni compounds and that the structure can often be convoluted into more than one peak. Therefore, a subtle change in the energy states of the Ni ions in the as-fabricated spinel due thermal aging could have promoted a different, but more stable ionic and 2p_{3/2}-satellite structure configuration.

Other possible explanations for change in Ni 2p level peaks include the effect of defects in the microstructure. Beard et al.¹⁷ have shown that order of magnitude increases in dislocation density in ammonium perchlorate caused increases in the FWHM of an XPS peak. However, very few, if any, dislocations were found in the thermistor material using transmission electron microscopy.¹⁸

Finally, there exists the possibility that incomplete inversion of the Ni occurred during fabrication with Ni²⁺ ions left in both tetrahedral (A-sites) and octahedral (B-sites).¹⁹ With suitable energy, Ni²⁺ ions migrate from B to A sites.¹⁹ Macklen⁸ determined the onset of this migration in Ni Mn₂O₄ to be 352°C. This mechanism might have also been active in the Ni-Fe-manganite at 300°C but how it relates to resistivity is still unclear. The Ni-Fe manganite ionic structure and the possibility of Ni²⁺ migration will be investigated further in the near future using neutron diffraction.

CONCLUSIONS

1. The only changes in the cation 2p_{3/2} peaks of the thermistor material that could be related to thermal aging at 300°C were those associated with the Ni ions. The 2p_{3/2} peaks for Mn, Fe, and O were unchanged.
2. Possible explanations for the changes in the Ni 2p_{3/2} peaks include:
 - (a) the migration of Ni²⁺ ions from octahedral to tetrahedral sites,
 - (b) subtle changes in the energy states of the Ni²⁺ ions which promoted a more stable ionic and 2p_{3/2} satellite structure, and/or
 - (c) the presence of Ni³⁺ ions, some of which revert back to Ni²⁺ upon aging.

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