X-ray Photoelectron Spectroscopy on thin magnesium and palladium layers

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Bachelor Thesis
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Abstract

For the research on hydrogen storage in magnesium, it is important to know the effects of oxidation on magnesium and if a thin palladium surface layer can prevent oxidation of the magnesium. I studied these effects with X-ray photoelectron spectroscopy (XPS), a surface analytical technique that uses a photon in electron out process based on the photoelectric effect. XPS provides an energy spectrum of the core electron bands of the elements present in the top nanometres of a sample. Oxidation can be detected as a shift in energy of the electron peaks.

The first experiments were performed to determine the basic properties of the experimental setup. After that, magnesium samples with and without palladium top layers were put in the air to measure the effects of oxidation on the samples. The results showed that a 3 nm palladium top layer prevents a magnesium sample from oxidation.

I also studied the effect of heating the samples. When a magnesium sample is heated to 180 °C, the surface looks different than before it was heated. XPS measurements showed a shift in the magnesium peaks as if the magnesium was oxidized. Heating of a magnesium sample with palladium top layer resulted in increased intensity of the magnesium peaks in the sample. This suggests that the palladium coverage decreases during the heating.

I also used XPS in a different experiment with dex-HEMA microspheres, little spheres that can transport medicines in the human body. Earlier experiments showed that the microspheres created a pHEMA surface layer. XPS measurements were performed to show the presence of such a layer. The results showed a uniform distribution of dextran and pHEMA at the surface, which indicates that the pHEMA surface layer wasn’t present in the measured microspheres.
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1. Introduction

Because of shrinking energy reserves, alternative energy sources and conversions are needed to keep everything running. Hydrogen could play an important role in the future as a way to store energy. The hydrogen can be used to power up cars, airplanes, boats, laptops and even in household appliance. Before hydrogen can be used fuel, it must be stored in a safe and efficient way. Storage in tanks can be dangerous and the hydrogen should be compressed a lot to make it volume efficient. Therefore researchers are looking for other ways to store hydrogen. A possibility is to store the hydrogen in a solid. Solids with a metal structure and enough space between the atoms can absorb hydrogen atoms. The hydrogen atoms can be released by heating the solid. This method of storing hydrogen can be much more volume efficient than compressing the hydrogen. There are several solids capable of storing hydrogen and research is performed with a lot of them. Magnesium is one of them.

In my research I looked at properties of samples with magnesium layers, sometimes with extra palladium top layers to prevent oxidation, with the experimental method called x-ray photoelectron spectroscopy (XPS). With this method a photon beam is pointed at a sample and photoelectrons are released by the photoelectric effect. By measuring the energy of the photoelectrons you can tell from what kind of atom they are released. XPS is a surface analytical technique that doesn’t infect the sample and gives information about the top nanometres of the sample surface.

I am a third year physics student and I performed this research as last part of my bachelor study. The research was performed in a period of a half year at the Debye Institute of the University of Utrecht. The research was attended by Govert Kruijtzer.

The aim of my research was to become familiar with the XPS technique and setup and to look at coverage, oxidation and heating of the magnesium and palladium samples. Main goal was to find the minimum thickness of the palladium top layer that totally covers the magnesium and that prevents oxidation of the magnesium. Besides my research on magnesium and palladium, I also performed some XPS measurements on dex-HEMA microspheres. This is a material that can be used to transport medicines into the human body. These measurements will be described in chapter 5.
2. Theory of XPS

The photoelectric effect

The physics behind XPS is based on the photoelectric effect. When a photon with a certain energy hits an atom, the atom sends out a photoelectron. If the energy of the photon is higher than the binding energy of the electrons in the atom, a photoelectron will escape from the atom. The kinetic energy can be measured with a spectrometer. Because atoms from different elements have different electron shells with different binding energies, the measurement of the kinetic energy of the ejected photoelectrons tells us from what kind of atom the electrons were emitted.

To calculate the binding energy of the electrons from the measured kinetic energy, we use the following energy conservation equation [2]:

\[ \hbar \omega + E_{\text{tot}}^i = E_{\text{kin}} + E_{\text{tot}}^f(k) \]  

\( \hbar \omega \) is the energy of the incoming photon, \( E_{\text{tot}}^i \) is the total energy of the initial state of the atom, \( E_{\text{kin}} \) is the kinetic energy of the photoelectron and \( E_{\text{tot}}^f(k) \) is the total energy of the atom after ejection of the photoelectron from the \( k \)th level. The binding energy of the photoelectron is defined as the energy required to remove it to infinity with a zero kinetic energy. In XPS measurements, the binding energy of an electron in the \( k \)th level compared to the local vacuum level, is defined as:

\[ E_{B}^V(k) = E_{\text{tot}}^f - E_{\text{tot}}^i \]  

This can be substituted in the conservation of energy equation (1):

\[ \hbar \omega = E_{\text{kin}} + E_{B}^V(k) \]  

Binding energies are expressed relative to a reference level. For the study of solids the Fermi level is used instead of the vacuum level, because the difference between the sample work function and the spectrometer work function causes a shift in the vacuum level between the sample and the detector. (Fig. 1). To prevent charging of the sample surface, the sample holder and the detector are in electrical contact. They are in thermodynamic equilibrium, so their Fermi levels are equal. From fig.1 the following energy equation can be deduced:

\[ \hbar \omega = E_{B}^\text{F}(k) + E_{\text{kin}} + \phi_{\text{spec}} \]  

\( E_{B}^\text{F}(k) \) is the binding energy relative to the Fermi level and \( \phi_{\text{spec}} \) is the spectrometer work function.

When analyzing insulators, the position of the Fermi level is uncertain and the sample surface can be charged. Therefore there can be an extra shift in the calculated binding energies, which can be compensated by using reference peaks in the measured spectrum.
After a photoelectron has been emitted from a core shell of an atom, there is a hole in the core atom shell of the atom. The hole can be filled by an electron from the M shell or valence band, with another electron from that shell carrying away the energy. This is an Auger process and the emitted electrons cause Auger lines in the XPS spectrum. The positions of these lines are also element specific, so they can also be used in the identification of the source atom.

**Information depth**

With XPS you can only analyse the top layer of a sample. The thickness of the layer that you can analyse is called the information depth. It depends on the ‘escape depth’ of the generated photoelectrons. The photons from the source have also a restricted free path in the sample, but it is much larger than that of the electrons, so it doesn’t restrict the information depth.

The escape depth of the photoelectrons depends on the inelastic mean free path (IMPF) of the electrons. This is the average distance that an electron with a given energy travels between successive inelastic collisions. After an inelastic collision, the electron is no longer useful for identifying the source atom, because it has lost a part of its kinetic energy. If it reaches the detector it will be a background count in the spectrum. The length of an IMPF depends on the properties of the solid and the energy of the electrons travelling through the solid. If elastic scattering effects are neglected, 95% of the measured electrons has its origin within three IMPF’s of the solid surface.

In earlier experiments the IMPF in different solids was calculated. I plotted the results as a function of the binding energy of the electrons (calculated for Al Kα source radiation)(fig. 2).
The plots show that the IMPF in magnesium is higher than the IMPF in palladium. The IMPF values in the solids that were used in the experiments are all between 1 and 7 nm. That means that the information depth should be between 3 and 21 nm, depending on which elements are in the surface layer.

**Chemical shifts**

The exact binding energy of an electron depends on the chemical environment of that element. For example electrons from SiO$_2$ have slightly different binding energies than electrons from Si and O. The energies of the core electrons, which are measured with XPS, are influenced by the Coulomb interaction with the other electrons and the attractive potential of the nuclei. Changes in the chemical environment cause a spatial redistribution of the valence electrons, which influences the measured binding energy of the core electrons. The shifts in binding energy are usually between 1 and 10 eV. The chemical shifts can be used to see what kind of chemical bindings the atoms in the sample have, for example if they are oxidized.

*Table 1: Theoretical binding energy used for the experiments. [1,3]*

<table>
<thead>
<tr>
<th>Element</th>
<th>1s</th>
<th>2s</th>
<th>2p</th>
<th>3d$_{5/2}$</th>
<th>4s</th>
<th>4p$_{3/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>1303 eV</td>
<td>89 eV</td>
<td>49.75 eV</td>
<td>335 eV</td>
<td>88 eV</td>
<td>52 eV</td>
</tr>
<tr>
<td>Mg oxide</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd</td>
<td>2p: 51.6 eV</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>285 eV</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>99.15 eV</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>103.4 eV</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Figure 2: Calculated IMPF for magnesium, magnesium oxide and palladium as a function of the binding energy of the electrons.*
3. Experimental setup

For XPS measurement we need an X-ray source, a sample holder with a sample and an electron energy analyzer. The X-ray source that was used was a Vacuum Generators XR2E2 Twin Anode with the standard Al/Mg anodes, where only the Al-K$_\alpha$ was operating. The spectra were recorded at a source power of 120 W. The analyzer was a CLAM-2 Hemispherical Analyzer with a mean radius of 100 mm. I used pass energies for the analyzer of 100 and 20 eV. The angle between the X-ray beam and the sample normal was 33.5$^\circ$ and the angle between the sample normal and the analyzer was 15$^\circ$ [4].

The obtained data from this setup is an energy spectrum with binding energies between 0 and 1486.6 eV. The upper limit is the energy of the photons of the Al K$_\alpha$ radiation. Before analyzing the data, the data was corrected for the spectrometer work function and the spectrometer transmission function. The work function (see chapter 2) is a linear function of the measured kinetic energy, which corrects the x-values of the measured spectrum. The transmission function corrects the y-values of the spectrum for differences in the sensitivity of the spectrometer depending on the kinetic energy of the electrons and the pass energy of the detector. After these corrections the spectrum was ready for analysis.

I used two methods to analyze the measured spectra. The first one is to plot the spectra in different ways and compare them with other spectra. The second one is to fit the data to Gaussian functions. To do this the the background had to be substracted. After the background subtraction, I fitted the data to one or more Gaussian peaks on theoretical positions.

For all the calculations in this chapter I used pre-written IDL functions. I had to change and rewrite some functions to improve the efficiency. The improved functions put the data in the right format to plot and fit the data to Gaussian functions.
4. Experiments

To understand the mechanics involving hydrogen desorption, it is of crucial importance to know the composition of the top layer of the solid used to absorb the hydrogen. First I performed two experiments to determine from what positions on the samples I got my information. I measured the size of the source beam and I measured the information depth in palladium. After that I looked at oxidized magnesium and the thickness of the palladium top layer to prevent oxidation of the magnesium. At last I heated my samples to 180° C where a structure change was expected, to find out what happened with the magnesium and palladium.

Size of source beam

To know at what positions of the samples I was measuring, I wanted to know the diameter of the source beam and the exact location where it hit the sample holder. For this experiment I used a clean silicon sample. In the y-direction the visible part of the sample was restricted by the sample holder, which contained silicon oxide. By shifting the sample holder in the y-direction, I should be able to locate the position of the edges of the sample holder from the ratio between the Si and the Si-oxide in the Si(2p) peak. Figure 4 shows the resulting spectra.

For my calculations I used the y-positions where the source beam was pointed just at the side of the visible sample surface (see figure 5). This is where the Si peak disappears and there is only Si-oxide in the spectrum. This is at y = 25.0 ± 1.0 mm and at y = 38.0 ± 1.0 mm (figure 4). The best position to measure spectra is in the

![Figure 4: Si(2p) peak of a clean silicium sample shifted in the y-direction. The left peak is from the Si on the sample and the right peak from the SiO₂ of the sample holder.](image-url)
middle between these edges at $31.5 \pm 1.0$ mm. The diameter of the source beam is the
difference between these edges minus the $y$-distance between the sample holder parts
($6.5 \pm 1.0$ mm), so the beam diameter is $6.5 \pm 1.0$ mm. For the $x$-position I did the
same measurements, but in the $x$-direction the sample holder is wider, so a quick
estimate for the best measuring position was sufficient.
In the $y$-direction the space between the sample holder edges is equal to the diameter
of the source beam, so it is very difficult to point the beam exactly on the sample
surface. Therefore there is always a possibility that the sample holder influences the
measured spectra, which can cause extra electron peaks.

**Information depth**

In the experiments presented here samples with magnesium layer with and without
palladium top layers were used. For the magnesium layers without palladium the
information depth is not important, because for those samples I need the information
directly from the surface. For the magnesium layers with palladium top layer the
information depth is very important, because I want to get information from the
magnesium layer under the palladium. If the palladium layer is too thick, I will only
see palladium in my spectrum and no magnesium. The theoretical inelastic mean free
path (IMPF) for palladium is between 0.8 and 2.5 nm, which should give an
information depth between 3.0 and 7.5 nm (see chapter 2).
There is only one peak in the magnesium spectrum that can distinguish magnesium
from palladium. The other peaks overlap with palladium peaks. This is the Mg(1s)
peak, theoretically positioned at 1303 eV (see chapter 2). To find the experimental
information depth, I measured the Mg(1s) for magnesium samples with palladium
layers of different thickness. Figure 6 shows the results.
For the magnesium sample without a palladium top layer the Mg(1s) peak is very
clear. In the spectra of the samples with a palladium top layer, there is a broad peak
between 1297 and 1311 eV. This is one of the auger lines of palladium. Only in the
spectra with the 3 nm palladium top layer the steeper Mg(1s) peak is still visible.
From these measurements I can conclude that the information depth for a palladium
top layer is between 3 and 5 nm at 1300 eV binding energy. This is a little higher then
expected in the theoretical model, because the theoretical IMPF for palladium at 1300
eV is approximately 0.8 nm. The measured information depth is a little more than 3
theoretical IMPF’s.
Figure 6: Mg(1s) peak of magnesium samples with palladium top layer. The thickness of the top layer is varied between 0 and 6 nm. The peak without top layer is scaled with a factor 0.5. The sharp peak on the right is the Mg(1s) peak. The wider and flatter peak is one of the auger lines of palladium.

Figure 7: Mg(1s) peak of a magnesium sample without palladium top layer after different periods in the air. When the magnesium oxidizes, the peak becomes smaller and shifts approximately 1 eV to higher binding energy.
**Oxidation of magnesium**

The aim of this experiment was to find the minimum thickness for the palladium top layer on a magnesium sample, which prevents oxidation of the magnesium. To do this, the palladium layer must totally cover the magnesium. Because the magnesium layer can be rough, the palladium layer should be at least a few nanometres.

I first had to know in what time scale magnesium normally oxidizes. I measured the Mg(1s) peak of a magnesium sample after different intervals in the air. The results are shown in figure 7.

Between 5 and 12 days in the air the Mg(1s) peak didn’t change much, so the for XPS visible surface of magnesium oxidizes in less than 5 days. Also important is that after one day a change in the peak is visible, which implies that it should be possible to see after one day if a magnesium sample oxidizes.

I measured a magnesium sample with a 3 nm palladium top layer before and after one day in the air. The result is shown in figure 8.

![Mg(1s) peak of a magnesium sample with a 3 nm palladium top layer before and after it was placed in the air.](image)

The Mg(1s) peak didn’t change after one day in the air, so the sample didn’t oxidize in that period. This implies that the 3 nm palladium top layer totally covers the magnesium and prevents it from oxidation.

**Heating of magnesium**

After heating a magnesium sample to 180°C the surface becomes a little whiter than before the heating. This could be caused by a change in structure of the magnesium. With XPS measurements before and after heating I tried to determine what happened exactly when the sample was heated.
Figure 9: Mg(2s) peak of a magnesium sample without palladium top layer before heating, after heating and after being placed in the air.

Figure 10: Mg(1s) peak of a magnesium sample with a 3 nm palladium top layer before heating, after heating and after being placed in the air.
The Mg(2s) peak of a magnesium sample that hasn’t been in the air before the measurement showed a shift of 1.8 eV after it was heated (figure 9). This can be caused by a change in the chemical environment of the magnesium. After the measurement, I placed the sample in the air for 24 hours. The XPS spectrum after that showed no chemical shift compared with the measurement after the heating. This implies that the sample didn’t oxidize in the air. An explanation for this is that the magnesium did bond to another element during the heating. The chemical shift during the heating can also be caused by a structure change of the magnesium. Both explanations change the chemical environment of the magnesium, but it is not likely that the structural change of the magnesium prevents oxidation.

I also heated a magnesium sample with a 3 nm Pd top layer (figure 10). After that the magnesium peaks in the XPS spectrum were much larger than before the heating and the palladium peaks smaller, which suggests that the palladium layer became thinner or didn’t cover all the magnesium anymore. Because the peak shape of the Mg(1s) changed during the heating, it is not possible to see if there was chemical shift. I placed this sample in the air too, which showed the same result as the sample without palladium. The peaks before and after didn’t change, so the magnesium didn’t oxidize.
5. Experiment with dex-HEMA microspheres

During my research I was requested to perform some XPS measurement on dex-HEMA microspheres. This experiment has no connection to the experiments with magnesium and palladium layers.

Introduction

Biodegradable polymeric microparticles are needed as controlled release delivery systems for pharmaceutical proteins in the human body. Hydrogels are often compatible with living tissue and proteins due their high water content. Therefore, hydrogel microspheres can be used as a delivery system. Hydroxy ethyl methacrylated dextran (short name: Dex-HEMA) microspheres degrade under physiological conditions and are compatible with living tissue, so they should be useful as delivery system. Dex-HEMA is formed out of two other materials, namely dextran and poly hydroxy ethyl methacrylate (pHEMA). Earlier experiments suggested that the dex-HEMA microspheres form an outer shell of pHEMA. The presence of such a layer could be proved with XPS measurements, where the spectra of the dex-HEMA microspheres are compared to the spectra of dextran and pHEMA. Normal dex-HEMA should have a ratio of 10/90 for the pHEMA/dextran distribution. If there is a layer of pHEMA at the surface, then the XPS measurements should show more pHEMA.

The experiment

The experiment was performed using the same XPS setup as for the magnesium and palladium experiments. The dex-HEMA microspheres were mixed with a small amount of water and the resulting paste was spread on a small plate to create a sample. The dextran and pHEMA samples were obtained by compression of powder. For the comparison of pHEMA and dextran the C(1s) peak in the XPS spectra was used, because the carbon atoms have different chemical environments in pHEMA and dextran molecules. The results of the XPS measurements are shown in figure 12. For the eye there is not much difference in the C(1s) peak of dextran and the dex-HEMA microspheres, but fitting results of the three peaks shows a presence of 10% of pHEMA in the spectrum.
of the dex-HEMA microspheres. This is the expected pHEMA/dextran ratio for the
dex-HEMA microspheres without the pHEMA outer shell.
The conclusion drawn from this experiment is that the dex-HEMA microspheres did
not have a pHEMA surface layer.

Figure 12: C(1s) peak in the XPS spectrum of pHEMA, dextran and the dex-HEMA microspheres.
6. Discussion

During the experiments there were various factors that could have influenced the results. In this chapter I will discuss the relevance of the results and conclusions.

The first experiments were to determine the properties of the experimental setup. The outcome was used for the further experiments. The first experiment resulted in an approximation of the size and position of the source photon beam. It showed that it is important to position the sample in the middle of the source beam. A shift of only one millimetre can cause extra peaks in the spectrum from the sample holder. The error in the beam diameter is 1.0 mm, because the position of the sample was shifted in steps of 1.0 mm during the measurements.

In the second experiment the experimental information depth was measured. Because I measured only three different palladium layers, the result was that the information depth is between 3 and 5 nm. The thickness of the palladium layers is based on earlier ERD-measurements on similar samples, which should have an error of less then 0.5 nm. The results differ minimal 5 nm from the theoretical model. This difference is not significant enough to reject the model.

After I determined the properties of the setup, I experimented with the oxidation of magnesium. There wasn’t a theoretical reference for the chemical shift of the Mg(1s) peak. Because that is the only peak that distinguishes magnesium from palladium, I had to measure the shift with a magnesium sample. The result showed a clear difference in the peak after one day in the air and a total shift of 1.0 eV after five days in the air. With this result I could conclude that a magnesium sample with a 3 nm palladium top layer doesn’t oxidize in one day. This can only be accomplished if the palladium layer totally covers the magnesium. A possible error in this conclusion can be caused by the short interval the sample was in the air, but the prior measurements showed that it is unlikely that the sample would oxidize after a longer interval.

Heating of the samples to 180 °C showed an unexpected result. For the magnesium sample without palladium top layer it caused a clear shift in the Mg(2s) peak. After the heating the sample didn’t oxidize in the air. Different processes could have caused this. The magnesium could have changed in structure, for example from amorphous to crystalline. This changes the chemical environment of the Mg atoms, so a chemical shift should be visible. It is unlikely that this structure change could have prevented the magnesium from oxidation. Another possibility is that the magnesium bonded to another element. This would cause a chemical shift and possibly prevented the magnesium from oxidation.

The heating of the sample with the 3 nm palladium top layer didn’t show a clear shift, because the magnesium peaks were too much distorted by the palladium. The intensity of the magnesium peaks increased significantly during the heating. Bonding of the magnesium and palladium atoms could have caused this. It is also possible that the sample surface became so rough that the palladium didn’t cover the magnesium anymore. Further experiments are needed to tell what happens exactly when the samples are heated to 180 °C.

The results of the experiment with the dex-HEMA microspheres stated a very clear conclusion. There was however not taken account of the possible errors in the spectra.
Because it were insulating samples, charging of the samples could have caused shifts in the energy spectrum. It wasn’t possible to compensate the shifts with the position of the C(1s) peak, because that peak was used to compare the samples. I don’t think that the results of this experiment were significant enough to reject the idea of the pHEMA surface layer.
7. References


