

The Open Gate Phenomenon

A Basis for New Energy Technologies

Susan Taft

Flowing Water Consulting

Dr. Jan Marwan

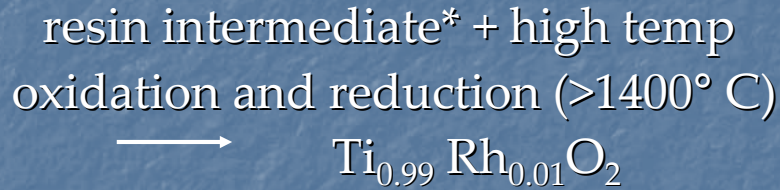
Dr. Marwan Chemie

1

Good morning, my name is Susan Taft. This presentation is about a unique solid-state phenomenon that results in significant and sustained electron transfer from an n-type semiconductor to Schottky metal particles that are grown from the semiconductor itself. It's what I call the Open Gate Phenomenon, the ultimate effect of which is that the metal particles behave as negatively charged electrodes without a conventional external power source.

The phenomenon was discovered from a failed experiment where we attempted to modify the bandgap of TiO_2 for use in a photoelectrochemical cell by substituting rhodium into the lattice. We ended up with completely unexpected data representing an unknown phenomenon.

Original Experiments



*resin intermediate based on Pechini process

2

In the original experiment, we used the Pechini process as the initial preparation step to produce a 1% (mole percent) rhodium substitution. The resin intermediate from the Pechini process was then subjected to high temperature oxidation and reduction in excess of 1400 C.

We chose X-ray Photoelectron Spectroscopy as an initial qualitative tool to determine the valence state of the rhodium to help determine whether rhodium was substituted into the lattice.

X-ray Photoelectron Spectroscopy

$$E_{\text{binding}} = E_{\text{photon}} - E_{\text{kinetic}} - \phi$$

- E_{photon} is the energy of the excitation radiation
- ϕ is the work function of the spectrometer

3

As a reminder, the key assumption is that the work function of the spectrometer and sample are aligned- are grounded.

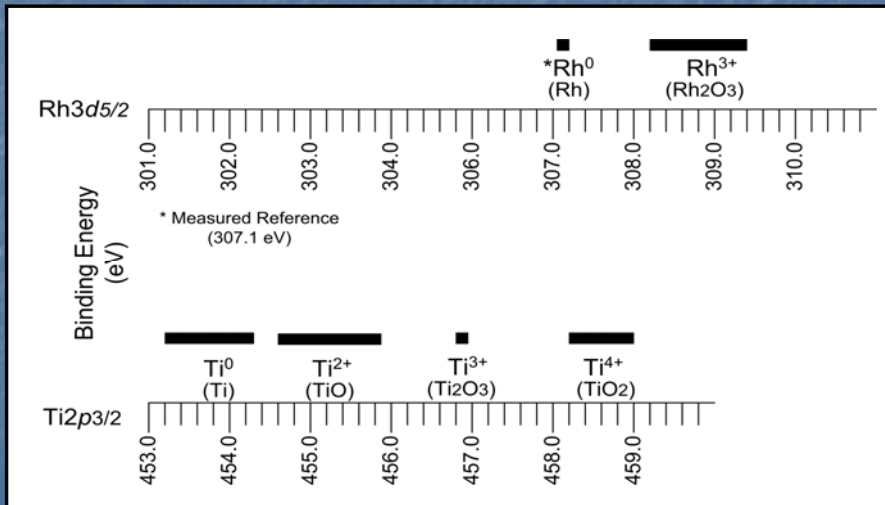
Binding Energy of an electron depends on

- Energy level from which it originates (*1s, 2s, 2p, 3s, etc...*)
- Oxidation state
- Local chemical and physical environment experienced by the electron

4

And of course, the binding energy of an electron depends on the energy level from which it originates, the oxidation state, and the local chemical and physical environment experienced by the electron.

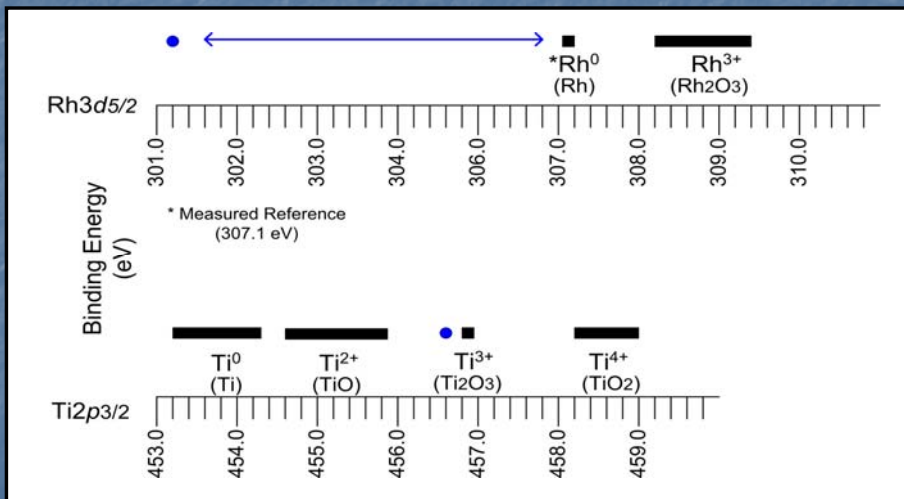
What we expected to see



5

We expected to see binding energies for rhodium in the vicinity of Rh³⁺ perhaps with a positive shift indicating Rh⁴⁺. Because of the reduction step, we expected binding energies for titanium to indicate a mixed valence oxide of Ti³⁺ and Ti⁴⁺.

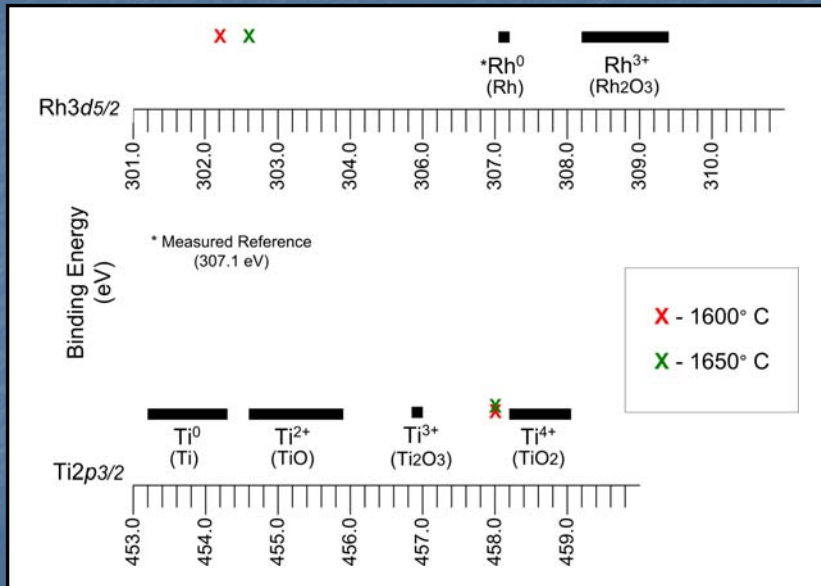
What we saw



6

What we saw was a negative binding energy shift of 5.9 eV below rhodium metal, or rather, the zero valence binding energy. At the same time, the binding energy for titanium had not shifted and instead indicated Ti^{3+} or rather, a reduced oxide.

Two Additional Materials



7

Two additional samples were analyzed which provided additional evidence that the data was real albeit very unusual. The next step was to examine the physical morphology of the materials.

Rhodium was not in the TiO_2 lattice
but in particles on the surface of TiO_2 :

- Particle shape was often a microsphere
- Found at grain boundaries
- In the 1 to 10 μm range

8

Using Scanning Electron Microscopy with Energy Dispersive X-ray microanalysis, we found that rhodium was not in the TiO_2 lattice but instead in particles on the its surface. The particles themselves were regularly and irregularly shaped microspheres, were often found at grain boundaries, and were in the 1 to 10 μm range. Although we failed to substitute rhodium into the lattice, the data was too strange and intriguing to ignore.

Other Observations

- Correlation of magnitude of binding energy shifts with metal particle size
- Persistence of binding energy shifts over time in spite of exposure to air

9

We prepared still additional materials and found a correlation of the magnitude of negative binding energy shifts for the metal particles with respect to their particle size; the larger the particles, the larger the shift. We also noted a persistence of binding energy shifts over time in spite of exposure to air.

Reported negative binding energy shifts for metals

- Surface atom core-level shifts (SCLS)
- Certain metal alloys
- Sub-monolayer thin film coverage and small clusters
- Strong metal support interactions (SMSI)

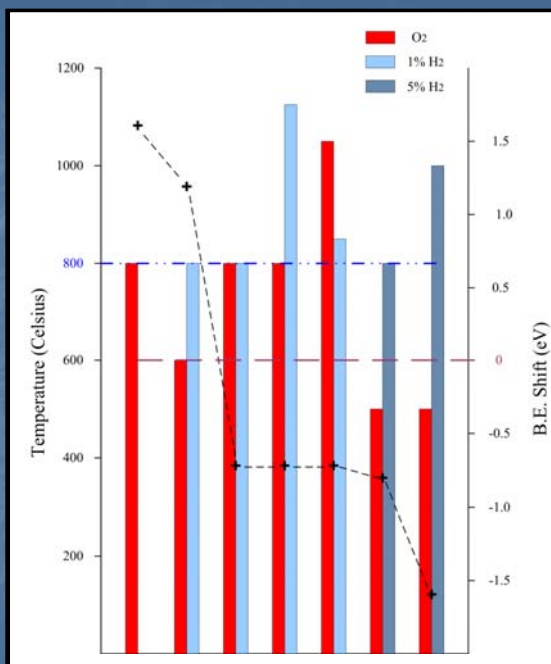
10

We conducted an extensive literature search and found four instances of negative binding energy shifts for metals, surface atom core level shifts, certain metal alloys, sub-monolayer thin film and small clusters, and strong metal support interactions. Without going to go into the details of each of these, suffice it to say that not only did the magnitude of the shifts of our materials far exceed these instances, but the differences in material preparation and the material-particle morphology precluded these explanations.

However, SMSI caught our attention. Strong metal support interactions is the term to describe unusual catalytic activity for metal particles on reduced oxide supports. We noted that the first materials in which SMSI was identified were platinum and rhodium (Group 8 metals) on reduced TiO_2 .

Binding Energy Shift for Rh3d_{5/2} Relative to Oxidation and Reduction Conditions

(0.5 weight percent Rh/TiO₂)

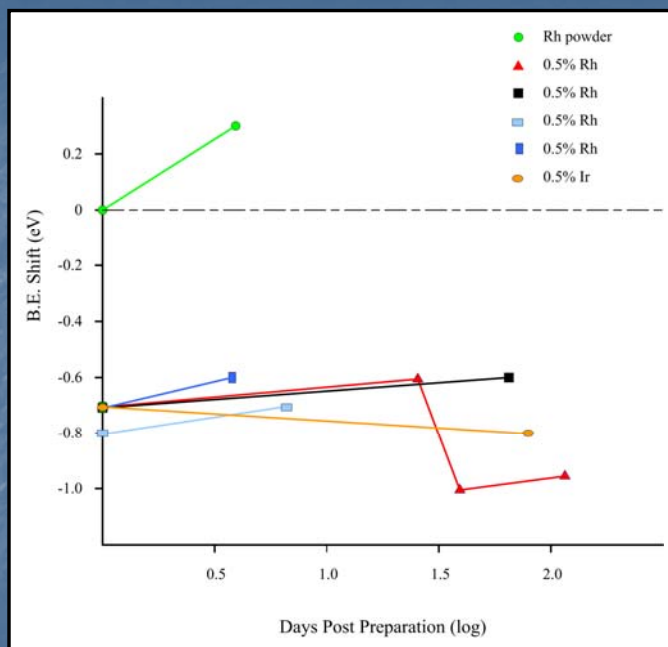


11

One of the questions we had was whether the negative binding energy shifts were dependent upon the initial Pechini process step. Although we saw no correlation with SMSI, the similarity of materials prompted us to use an impregnation-evaporation process (commonly used to prepare catalyst materials) as a replacement for the Pechini process step. Using this replacement process, we then subjected the materials to varying high temperature oxidation and reduction temperatures and reducing environments with respect to obtaining negative binding energy shifts. What we found was a lower threshold of approximately 800 C (depending upon the reduction environment) which we correlated with rutile transformation of the TiO₂. It should be noted that rutile transformation temperature is dependent upon the synthesis method, reducing environment (in argon, hydrogen, or a vacuum), and the presence of other ions. We concluded that negative binding energy shifts were linked to rutile transformation.

We also prepared materials with iridium and platinum and observed negative binding energy shifts of 0.7 eV below zero valence values for the metals. This was consistent with our observations for rhodium given the same particle sizes and verified that the negative binding energy shifts were not exclusive to rhodium.

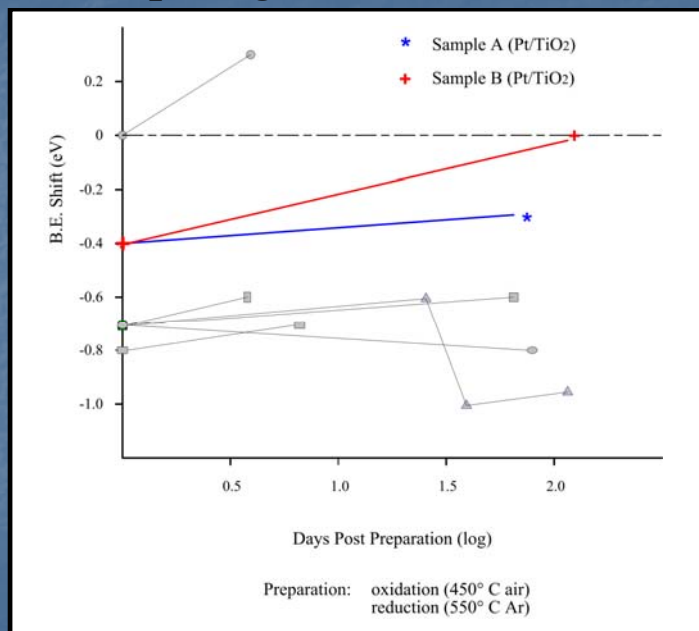
Duration of Negative Binding Energy Shift



12

We continued on-going examination of some of the materials and found persistent negative binding energy shifts for up to 128 days. We also prepared a rhodium powder reference using a high temperature reduction temperature and environment. On Day 1 (the day after its preparation), the binding energy indicated we had metallic rhodium- no binding energy shift was observed. However, by Day 5 with air exposure we observed a positive shift of 0.3 eV indicating the presence of surface oxides which is in stark contrast to our materials. It should also be noted that at no time was a positive shift of that magnitude (0.3 eV) observed in our materials. We concluded that no surface oxidation had occurred.

Spichiger-Ulmann Data



13

One SMSI paper caught our attention in regard to the persistence of negative binding energy shifts. The paper was published in the proceedings of the 1986 ACS symposium about SMSI. The Spichiger-Ulmann paper reported a persistence of negative binding energy shifts in spite of exposure to air, for 75 days for one sample and for another, a positive shift at four months. This paper is an anomaly in this regard among the multitude of SMSI papers published in the past 25-30 years.

Although their preparation was different than ours (as well as from many SMSI studies- a platinumized thick film TiO₂ on titanium metal) and the oxidation and reduction temperatures were below those used in our studies, it was still consistent with rutile transformations which can occur as low as 400 C, again depending upon the synthesis method, reducing environment (argon, hydrogen, or vacuum), and the presence of other ions.

What is significant is that this provides additional corroboration of our data.

Sufficiently high temperature oxidation and reduction resulting in

- Transformation to rutile TiO_2
- Reduction of TiO_2 to a mixed valence oxide

14

At this point all of the results brought us to conclude that obtaining negative binding energy shifts required a sufficiently high temperature oxidation and reduction that results in the transformation to rutile TiO_2 and its reduction to a mixed valence oxide.

The metal particles *grow from*
a TiO_2 substrate
in contrast to a deposition *onto*
a TiO_2 support.

15

This preparation allows the metal to grow from the TiO_2 substrate in contrast to a deposition onto a TiO_2 support. This implies inherent differences between the metal-substrate interface and the metal-support interface and is critical to understanding the mechanism that results in negative binding energy shifts.

Group VIII metals on reduced TiO_2 are a Schottky metal on an n-type semiconductor which results in a *rectifying (one-way) junction*.

This junction is *critical* to understanding the negative binding energy shifts.

16

Group 8 metals on reduced TiO_2 are a Schottky metal on an n-type semiconductor which results in a one-way or rectifying interface. Based on their respective work functions, electrons flow from TiO_2 into the metal. For our materials it also means that the particles and the substrate are not at the same potential because of the rectifying junction-interface.

XPS and Binding Energy

The assumption is
that the Fermi levels *should align*.

The rectifying junction
interferes with alignment for the *metal particles*.

The negative charge on the particles
is the local environment
and *results in*
negative binding energy shifts.

17

For determining binding energies by XPS, the assumption is that the Fermi levels of the spectrometer and sample should align. However, the rectifying junction interferes with this for the metal particles. Therefore, the negative charge on the particles is the local environment that results in negative binding energy shifts. XPS is measuring that negative charge on the particles.

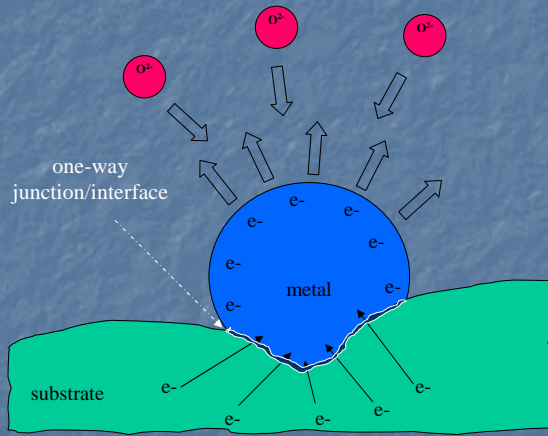
The negative charge on the particles
is the result of a *unique interface* between the
Group VIII metal,
(a Schottky metal)
and reduced rutile TiO₂
(an n-type semiconductor).

18

So what does this really mean? The negative charge on the particles is the result of a unique interface. It is unique because the metal is grown from the substrate and because of this, it significantly affects the Schottky barrier height and charge neutral zone. The interface actually allows the negative charge to accumulate on the metal particles and not solely at the interface itself.

Our observations indicate that the electron flow into the particles appears to initiate during high temperature reduction and is of sufficient magnitude to change the metal particle morphology- to that of a sphere. This makes perfect sense since a sphere is the preferred shape to equalize charge interaction.

Cathodic Protection



19

The ultimate effect of the negative charge on the particles is that it provides cathodic protection from surface oxidation. Herein is the crux of its significance: the metal particles appear to behave as negatively charged electrodes with a conventional external power source.

What is clear is that what we know of traditional metal-semiconductor interfaces does not completely apply here where the metal is grown from the semiconductor itself.

Although the mechanism is not based in electrochemistry, there is much we don't know. But it begs the question, is the mechanism analogous to electrochemistry except based on work functions instead of electrode potentials? Which then leads to the next question: are we actually looking at a new mechanism for the direct generation of electricity?

Electrochemical Applications for Phenomenon-Based Materials

- Electrocatalysts for fuel cells
 - Shift toward more anodic potentials
 - Reduction of noble metal use through alloying
 - Increased CO-toleration
- Sensors
 - Increased CO-toleration and other poisoning
- Other catalysts and electrocatalysts
 - Other metal/reducible metal oxide systems

20

Needless to say, many questions remain unanswered at this point. But while it is not based on electrochemistry, there are nevertheless many potential energy and non-energy applications based on phenomenon-based materials.

The benefits as an electrocatalyst for fuel cells would be a shift toward more anodic potentials, reduction of noble metal use through alloying, and increased CO-toleration. Sensors would benefit from the same CO and poisoning tolerations. Additionally, there may be other metal/reducible metal oxide systems which could be prepared to exhibit the same phenomenon. This opens the possibility for even more applications for phenomenon-based catalysts and electrocatalysts.

The Open Gate

21

In conclusion, the Open Gate hypothesis is by no means the final word on this unusual phenomenon. We have only scratched the surface of what we know. Much more research is needed. However, I believe the Open Gate Phenomenon is a game changer.

We hope that this presentation will encourage you and others to explore this phenomenon, and in particular, its potential for new energy technologies.