INTERACTION OF THE ELECTROMAGNETIC RADIATION WITH
THE SURFACE OF PALLADIUM HYDRIDE CATHODES

E. Castagna, S. Lecci, M. Sansovini, F. Sarto and V. Violante RdA

ENEA, C. R. Frascati
Nuclear Fusion and Fission and Related Technologies Department
Via Enrico Fermi, 45 - 00044 Frascati (Rome) ITALY

The change of the electronic density of metallic Pd due to the hydride formation and to the build-up of the double layer, rising at the metal-dielectric interface when an electric field is applied, is involved in the variation of the metal dielectric function. A model including also metal surface roughness has been developed to take into account such modifications.
Interaction of the Electromagnetic Radiation with the Surface of Palladium Hydride Cathodes

E. Castagna, S. Lecci, M. Sansovini, F. Sarto and V. Violante RdA

ENEA. C. R. Frascati
Nuclear Fusion and Fission and Related Technologies Department
Via Enrico Fermi, 45 - 00044 Frascati (Rome) ITALY
Introduction

- The dissolution of hydrogen within a metal lattice and the formation of a metal hydride greatly perturb the electrons and phonons of the host material. Several are the relevant observed effects

  - The generally observed expansion of the lattice, often including a change in the crystal structure, involves a modification of the symmetry of the states and a reduction of the band width.

  - The attractive potential of the protons affects those metal wave-functions which have a finite density at the H site and leads to the so called metal hydrogen bonding band below the metal d-band.

  - The additional electron brought by the H atoms into the unit cell produces a shift of the Fermi level.
Consequently, the electronic Density of State of Palladium changes as deuterium solubilized inside metal lattice increase.

Fig. 1 - Total Density of States at the Fermi level plotted versus hydrogen concentration in PdHx
The electrochemical interface is well represented by a double layer structure in contact with a space of charges.
\[
\frac{d\varphi}{dx} = -\left(\frac{8KTn_0}{\varepsilon_0}\right)^{1/2} \sinh\left(\frac{ze\varphi}{KT}\right)
\]

\[
\varphi = \frac{2KT}{ze} \ln\left(\frac{1 + \beta e^{-\tilde{k}x}}{1 - \beta e^{-\tilde{k}x}}\right)
\]

\[
\varphi_2 = \varphi_0 + \left(\frac{d\varphi}{dx}\right)_{x=x_2} x_2
\]

\[
\sigma^m = \left(8KT\varepsilon_0 n_0\right)^{1/2} \sinh\left(\frac{ze\varphi_2}{2KT}\right)
\]

\[
\tilde{k} = \left(\frac{2n_0 z^2 e^2}{\varepsilon_0 kT}\right)^{1/2}
\]

\[
E_{dl} = \left.\frac{d\varphi}{dx}\right|_{x_2}
\]

\[
\beta = \tanh(ze\varphi_0 4KT)
\]

\[
\varphi_0 = 250 \text{mV}
\]

\[
\sigma^m = 10^{14} \text{ C/m}^2
\]

\[
E_{dl} = 10^8 \text{ V/m}
\]
The purpose is to obtain a reasonable, consistent dielectric function value suitable to be used in our model.

Double layer is characterized by a high density of charges: it is necessary to describe a metal foil having on its surface a very high charge density, which results in an intense electrostatic field.
The dielectric function variation related to surface charge density is

$$
\Delta \varepsilon_{PdH_x} = (\varepsilon_{x_{\text{free}}} - 1) \frac{\Delta N \varepsilon_{PdH_x}}{N e_{PdH_x}}
$$

$$
\Delta N e_{PdH_{0.99}} = \frac{\sigma^m}{q \cdot d}
$$

$$
N e_{PdH_x} \approx \frac{2 DOS \cdot KT}{Ry} \frac{1}{V_{cell}}
$$

$$
\Delta \varepsilon_{PdH_x} = \varepsilon_{PdH_x} + \Delta \varepsilon_{PdH_x}
$$

$$
d = \frac{c}{\sqrt{8\pi\mu_{0Pd} \rho_{PdH_{0.99}}}}
$$

---

Fig. 4 - PdH0.99 dielectric function real component versus angular frequency. The shift to negative values due to surface charge is shown.

Fig. 5 - PdH0.99 dielectric function imaginary component versus angular frequency. The shift to higher values due to surface charge is shown.
Surface Plasmons

- Surface plasmons (polaritons) are quanta of plasma oscillations created by the collective oscillation of electrons on a solid surface.

- Surface plasmons may be generated by mechanisms able to produce charge separation between Fermi level electrons and a background of positive charges (i.e. lattice atoms).

- Surface Plasmons Wave Vector x component dispersion relation is expressed by

\[ K_x = \frac{\omega}{c} \sqrt{\frac{\varepsilon_d \varepsilon'}{\varepsilon_d + \varepsilon'}} \]

- Under certain conditions one could use the simplified expression:

\[ K_x' = \frac{\omega}{c} \sqrt{\frac{\varepsilon_d (\omega^2 - \omega_p^2)}{\omega^2 (\varepsilon_d + 1) - \omega_p^2}} \]

\[ \omega_p^2 = \frac{Ne^2}{m_{\text{eff}} \varepsilon_0} \]
Surface Plasmons Excitation Conditions

- Prism Coupling

\[ K_x = \frac{\omega}{c} \sin \theta \pm \Delta K_x = K_{sp} \]

- Roughness Coupling

\[ K_x = \frac{\omega}{c} \begin{cases} \frac{\epsilon_d \epsilon' - \epsilon behaved}{\sqrt{\epsilon_d + \epsilon' behaving}} & \epsilon_d + \epsilon' > 0 \\ \frac{\epsilon_d + \epsilon' behaving}{\sqrt{\epsilon_d - \epsilon behaved}} & \epsilon_d + \epsilon' < 0 \end{cases} \]

\[ K_x = \frac{\omega}{c} \frac{\epsilon_p}{\sin \theta} \]

Fig. 6 - Matching condition given by interception between s.p. and laser beam dispersion law, achievable using a prism coupler.

Fig. 7 - Matching condition given by laser beam wave vector increment due to a corrugation lattice.
Surface Plasmons resonance could give rise to a huge local field enhancement, due to a focusing effect: a broad e.m. wave is confined in a surface.

This phenomenon could be understood considering the wave vector component perpendicular to the interface between the two media:

\[
K_{z2} = \frac{\omega}{c} \sqrt{\frac{\varepsilon_2^2}{\varepsilon + \varepsilon_1}}
\]

\[
K_{z1} = \frac{\omega}{c} \frac{\varepsilon_1}{\sqrt{\varepsilon + \varepsilon_1}}
\]

The field enhancement could be in a phenomenological way expressed as:

\[
\frac{\left| \vec{E}_j \right|^2}{\left| \vec{E}_0 \right|^2} \approx \frac{K_{zj}''}{K_x''}
\]
Enhancement of about $10^2$ factor could be obtained in this classical calculation. On appropriate structures and by quantum mechanical computation the enhancement factor could be equal to several magnitude orders.

Fig. 8 - Electromagnetic Field due to SP excitation, arbitrary units
Palladium Cathodes Roughness

L72a(207-225)RA_4.jpg

L68(0-20)RAE_5.jpg

L68(20-40)RAE_3.jpg

L51(43-81)RAE_5.jpg
<table>
<thead>
<tr>
<th>Sample</th>
<th>Roughness (μm)</th>
<th>Surface Profile</th>
</tr>
</thead>
<tbody>
<tr>
<td>L72a(207-225)RA</td>
<td>0.024</td>
<td>2</td>
</tr>
<tr>
<td>L68(0-20)</td>
<td>0.109</td>
<td>2.3</td>
</tr>
<tr>
<td>L68(20-40)</td>
<td>0.175</td>
<td>3</td>
</tr>
<tr>
<td>L51(43-81)RAE</td>
<td>0.112</td>
<td>1.8</td>
</tr>
<tr>
<td>L55(215-254)RAE</td>
<td>0.132</td>
<td>1.6</td>
</tr>
<tr>
<td>L56(6-26)RAE</td>
<td>0.205</td>
<td>1.5</td>
</tr>
</tbody>
</table>
A surface Plasmon can not be excited by direct impinging of an electromagnetic radiation on a smooth surface

A rough surface increases incoming electromagnetic wave momentum

Modelling: Laser Angular Reflectance from gratings

- **Deepenings**

S10_O3
Roughness=0.175µm
A.W.L.= 3µm

Roughness=0.112µm
A.W.L.= 1.8µm

Roughness=0.132µm
A.W.L.= 1.6µm

Roughness=0.205µm
A.W.L.= 1.5µm
Finite Element Method Model

- **Previous Model:**
  - No information on Electromagnetic Field localization
  - Source terms can not be included in the Analytical Model

- **FEM implemented to solve differential Maxwell equations.**

- **Adequate boundary conditions are needed:** Perfectly Matched Boundary Conditions (PML)

---

**Fig. 9** - Electromagnetic Wave propagation in free space

**Fig. 10** - Plane wave propagating in a two semi-infinite media domain

**Fig. 11** - The domain of interest is surrounded by outer PML elements.
Fig. 12- Magnetic field originated by a surface current flux

Fig. 13- Electric field distribution originated by an alternate surface current density flowing on a corrugated interface between air and PdHx
Conclusions

- Description of Pd samples surface under cathodic polarization has been performed by including the effects of high charge density at the inter-phase.

- On suitable surfaces electron plasma oscillation may occur. Their frequency is depending on the material electronic properties and surface profile properties.

- The models developed show that under adequate conditions strong electromagnetic field localization and magnification arises.

- Advanced modelling of process occurring at the interface and into the bulk is the first step towards material engineering.