Ab initio modeling of Cs-Mo interfaces in negative ion sources.

A Damone[1], A Panarese[2], C M Coppola[1,3,4], J Jansky[1,5], C Coletti[6],
L Chiodo[7], G Serianni[8], V Antoni[8] and <u>S Longo</u>[1,2,4]

[1]*Department of Chemistry, University of Bari, via Orabona 4, 70126 Bari, Italy*
[2] *CNR-IMIP, Bari Section, via Amendola 122/D, 70126 Bari, Italy*
[3] *Physics and Astronomy Department, University College London, London WC1E 6BT, UK*
[4] *INAF-Osservatorio Astrofisico di Arcetri, Largo E. Fermi 5,I-50125 Firenze, Italy*
[5] *Department of Physical Electronics, Masaryk University, Faculty of Science, Kotlarska 2, 611 37 Brno,
Czech Republic*
[6] *Dipartimento di Farmacia, 'G. d'Annunzio' University, Via dei Vestini 31, 66013 Chieti, Italy*
[7] *ETSF, Center for Life Nano Science at Sapienza, Istituto Italiano di Tecnologia, Viale Regina Elena
291, I-00161, Roma, Italy*
[8] *Consorzio RFX, Corso Stati Uniti, 4 35127 Padova, Italy*

The paramount relevance of Cs as a catalyst in negative ion sources used in nuclear fusion studies is not balanced by an appropriate knowledge of the microphysical properties of Cs interface with high performance metals in this field, particularly Mo. In this study the interaction of Cs with Mo under conditions of interest for negative ion sources is studied using different methods. A Cs–Mo potential is formulated for Cs interaction with Mo in gas phase and Mo[001]. Mo–Mo and Cs–Cs potentials are based on new fits of the data present in the literature. The use of these potentials is illustrated by classical MD calculations for Cs partial layers on Mo[001]. In perspective this study can contribute with sound physical data to the ongoing effort to improve the performance of Cs catalyzed negative ion sources.

1. Introduction

Cs is the most well known catalyst used in negative ion sources for fast neutral beam generation employed in nuclear fusion, where the element is evaporated and deposited on Mo surfaces forming non permanent films [1,2]. Its action is effective for the most important negative ion formation channel, namely the surface process, where hydrogen (deuterium) atoms and positive ions like H_2^+ are converted into negative H^- ions by interacting with the surface. The conversion yield depends on the work function of the surface, which is found to be lowered by caesium deposition on metallic surfaces. The use of Cs is complicated by several issues related to its transport inside the device which in turn needs realiable data for the adhesion energy of Cs on wall surfaces, sticking coefficients and surface diffusion: all these issues cannot be clarified without a sound microphysical understanding of the Cs-Mo interaction.

Although a few papers in the past have considered specific issues [3-6], the present importance of this system asks for state-of-the-art, integrated study of closely related issues like Cs–Mo interaction, film morphology, interaction potentials, adhesion energy. These studies are made complex by their microphysical nature, which requires the use of quantum mechanical methods and by the circumstance that real Cs layers are never perfect and the developed method must be flexible enough to include partially disordered layers of any thickness.

Work is in progress by the present collaboration to apply state-of-the-art techniques to the microphysical studies of this system. The results produced until now include a view of the actual structure of an incomplete layer of Cs atoms on a Mo surface, estimates of the adsorption energy, essential for thermophysical macroscopic models as well as to experimentalists to improve source performance and a new potential for Cs-Mo interaction [7].

2. Calculation method

Ab-initio methods are used to obtain results for microphysical data consistent with quantum mehanics.

The interaction of single atoms of Cs and Mo (a CsMo molecule) is studied in gas phase using the Coupled Cluster (CC) method. This method allows to study the binary (gas phase) interaction with high accuracy and it provides information on the appropriate shape for the interaction potential of Cs atoms with Mo surfaces. Density Functional Theory (DFT) calculations on a reduced cell are used to

determine the adsorption energy of Cs on Mo for different sites. These calculations are performed using the plane-wave, pseudopotential based code Quantum Espresso.

Based on this information, a fit of the Potential Enrgy Surface (PES) for a single Cs atom interacting with the whole Mo[001] surface is developed.

The classical Molecular Dynamics (MD) method is used to determine the equilibrium morphology of the film of Cs on Mo at definite temperature from the developed potential energy and to estimate transport coefficients.

As regards Cs-Cs and Mo-Mo, appropriately optimized binary potentials are found to provide satisfactory results (e.g. crystal data for Mo).

The *total* potential energy of the system to be used in the MD is the sum, for all simulated atoms, of (1) binary Cs-Cs contributions (2) binary Mo-Mo contributions (3) the Cs-surface and Mo-Cs contributions. After the total energy U is determined, the force acting on any single atom i is determined as $-\partial U/\partial r_i$. To keep the surface at the required temperature T_0 a "casing" of additional Mo atoms surrounding the Mo surface is introduced [7]. Atoms of this casing are kept at T_0 by an additional viscous force which is proportional to $(T-T_0)/T_0$.

In order to reproduce a typical disordered layer, the positions of the Cs atoms are randomly generated in the space over the Mo[001] substrate and the velocities are sampled by a Maxwellian distribution. Periodic boundary conditions are used for Cs atoms, so that 8 cell replicas are included for both the adsorbed and gas phase. The molybdenum substrate consists of 5 layers with 563 particles with body-centered cubic symmetry, exposing the [001] face.

3. Sample of results

In Table 1 values of the energies and the distances obtained for different sites using the DFT code are reported. Three different, symmetrical adsorption sites for Cs atoms on the Mo[001] surface are considered.

Adsorption site	E_{ads}^{PBE} [eV]	d_{Cs-Mo} [Å]
Top (4 × 4)	2.59	3.5
Hollow (4 × 4)	2.78	3.9
Bridge (4 × 4)	3.00	3.7

Table 1. Calculated adsorption energy and Cs-Mo distance for a 4x4 Mo cell and different sites.

Calculations produce values of the adsorption energy Cs-Mo[001] much higher than for pure Cs.

This result is important for studies of Cs transport in negative ion sources since it affect Cs evaporation and surface diffusion.

Next, sample results of the final stage of the process are reported: the application of the potentials to classical dynamics simulations of the interface.
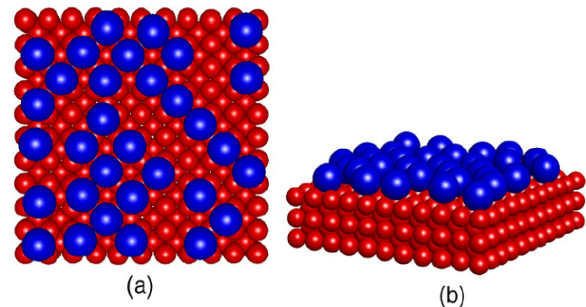

Figure 1. Graphical rendering of MD results for Cs atoms on Mo[001]: (a) top view, (b) side view.

Figure 1 shows a graphical rendering of the morphology of Cs partial layer on Mo. The rendering is based on a representation in which each atom is a sphere with a radius equal to the metal radius for Cs and Mo respectively. The BCC Mo structure is represented below, while the largest spheres are Cs atoms. The interface displays a peculiar structure associated to the large difference in metal radii, which may affect the catalytic and transport properties of Cs in negative ion sources.

5. References

[1] Hemsworth R S, Tanga A and Antoni V 2008 *Rev. Sci.Instrum.* **79** 02C109

[2] Taccogna F, Minelli P, Diomede P, Longo S, Capitelli M and Schneider R 2011 *Plasma Sources Sci. Technol.* **20** 24009–15

[3] Soukiassian P, Riwan R and Borensztein Y P 1982 *Solid State Commun.* **44** 1375–8

[4] Chubb S R, Wimmer E, Freeman A J, Hiskes J R and Karo A M 1987 *Phys. Rev.* B **36** 4112

[5] Soukiassian P *et al* 1985 *Phys. Rev.* B **31** 4911

[6] Soukiassian P *et al* 1985 *J. Phys. C: Solid State Phys.* **18** 4785

[7] Damone, A., et al. *Plasma Physics and Controlled Fusion* 57.3 (2015): 035005.