INFLUENCE OF OXYGEN VACANCIES AND 26 D-IMPURITY ON ELECTRONIC AND TRANSPORT PROPERTIES OF ZIRCONIA

Natalya Tokiy, Tatyana Konstantinova, Valentine Tokiy* and Diana Savina
Donetsk Physical&Technical Institute NAN Ukraine
Donetsk, str. R. Luxemburg 72, 83114 Ukraine
Donetsk Institute of Social Education
Donetsk, Universitetskaya, 2, 83000 Ukraine

ABSTRACT

The present work is dedicated to the simulation of the electronic structure of 26 different impurity d-elements (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Y, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Lu, Hf, Ta, W, Re, Os, Ir, Pt, and Au) and transport properties of zirconia using the tight-binding theory. The problem has been considered in the framework of the cell method and the band calculations. During simulation, the impurity is placed in the substitutional site of zirconium. The calculations have shown that the oxygen vacancy in zirconia is a split vacancy. We have established that the migration barrier for oxygen in zirconia sharply decreases with Cu, Ag, Ni, Pd, Pt and Au-doping.

INTRODUCTION

Stabilized zirconia ceramics are widely used (fuel cells, oxygen sensors, refractories, etc.) and are intensively studied materials because of their outstanding electrical properties. Worldwide efforts to commercialize solid oxide fuel cells (SOFCs) involve the investigation of numerous stacking principles as well as cell designs. First, complete cells for SOFC stacks typically are produced in two designs: 1) electrolyte-supported cells or 2) electrode-supported cells. Both types of cells are applicable for high-temperature SOFC stacks. For low-temperature operation, the resistance of a thick electrolyte renders the electrolyte-supported design unattractive because of a thermal activation energy of ~0.8 eV for oxide ion conductivity in the preferred electrolyte material, stabilized zirconia (1).

Second, the cells must exhibit a number of features, mainly a fairly high mechanical strength for handling and mounting, sufficient in-plane conductivity, a low polarization resistance, and good durability. Zirconia (ZrO$_2$) doped with oxide metals forms an important family of solid electrolytes. These materials are commonly used in a variety of advanced technologies such as oxygen sensors and fuel cells. The effect of the dopant oxide on the ionic conductivity in ZrO$_2$-based binary systems has been investigated extensively.

Third, the fuels of nuclear power-producing stations are the ceramics UO$_2$ and the so-called mixed oxide MOX, i.e., (U, Pu) O$_2$. Today, inert matrices are investigated. These matrices are also ceramics to replace the UO$_2$ to avoid forming new actinides. Candidate
material is stabilized cubic ZrO$_2$ (2). A mechanism to explain the stabilizing influence of oxygen vacancies is not available at present and needs to be considered from a fundamental microscopic level. That is why a theoretical analysis of the electronic structure of cubic ZrO$_2$ with the vacancies is necessary. On the other hand, the sintering, diffusion creep, and oxidation of zirconia at high temperature are determined by vacancy mobility, which also makes calculating the energy of migration of oxygen vacancy important. We have begun these calculations on the influence of doping on electronic structure of zirconia in the framework of cell models (3,4). The theoretical analysis of the electronic structure of zirconia-containing vacancy and split vacancy has been carried out (5,6). In the present work, we show some of the latest results. In (3), calculations are given for cluster modeling of the electronic structure of the oxygen vacancies in cubic ZrO$_2$.

Our previous work (7) was dedicated to the cell simulation of the electronic structure of 26 impurity d-elements (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Y, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Lu, Hf, Ta, W, Re, Os, Ir, Pt, and Au) and activation energies of dehydrogenation of Y-stabilized zirconia nanolayers. This model of a plate-like amorphous zirconia is supplemented from above and below by planes of hydrogen atoms located above and below the atoms of oxygen. For calculating energy levels of a plate of zirconia covered by hydrogen we used a cell of 20 atoms: 4 Zr atoms, 8 O atoms, and 8 H atoms. Our approach is to lay down periodic boundary conditions on a cell in the 111 plane. The plates are, of course, hypothetical with respect to both composition and structure. By definition they have the same lattice period and, moreover, show an ordered arrangement of Me atoms (in reality, these may be distributed within their sublattice statistically). A rough estimate of the bonding energy for the hydrogen and zirconia plate was obtained by monitoring the sum of the energies of all the occupied one-electron molecular orbitals of the cell at removing hydrogen. We established that the change in a charge state of impurity center plays a determining role in the influence of an impurity on thermal desorption of hydrogen from the zirconia surface. As calculations show, the activation energy of thermal desorption of hydrogen from a plate of zirconia grows sharply at chromium doping. The predicted influence of impurities on the process of thermal desorption of hydrogen from the surface of zirconia plate-like nuclei is in agreement with the experimentally met difficulties in the formation of nanocrystalline particles as a result of doping with chromium (8).

This work is dedicated to simulating the electronic structure of the 26 impurity d-elements and activation energies of diffusion of oxygen in the zirconia using the tight-binding theory.

**MODEL STRUCTURES USED IN THE CALCULATION**

The small primitive cell corresponding to the chemical formula of Zr$_8$O$_8$ and characterized by the translations (1,0,0), (0,1,0) and (0,0,1) was chosen deliberately. As a basis for modeling the diffusion process in crystal zirconia, we take the model structure of cubic zirconia used in our work (5,6). The primitive cells of the Zr$_4$O$_7$V, Zr$_3$MeO$_7$V, Zr$_7$O$_6$VsO, and Zr$_3$MeO$_4$VsO crystals were constructed from the initial cell in the simplest way: the first and second by substituting V for one of the eight O atoms and the
third and fourth cell by substituting two V for the two nearest neighbor O atoms and the interstitial atom O between vacancies. The latter are split vacancy configuration V's.

Table 1. Atomic Coordinates of Samples Investigated (in units of primitive cell rib).

|          | Zr₄O₈ | Zr₄O₇V | Zr₃MeO₇V | Zr₄O₅VsO | Zr₃MeO₆VsO |
|----------|-------|--------|----------|----------|------------|
| Me       | 0,0,0 | 0,0,0  | 0,0,0    | 0,0,0    | 0,0,0      |
| Zr       | ½,0,½ | ½,0,½  | ½,0,½    | ½,0,½    | ½,0,½      |
| Zr       | ½,½,0 | ½,½,0  | ½,½,0    | ½,½,0    | ½,½,0      |
| Zr       | 0,½,½  | 0,½,½  | 0,½,½    | 0,½,½    | 0,½,½      |
| O        | -¼, ¼,¼ | V       | V        | Vs       | Vs         |
| O        | -¼, -¼, -¼ | ¼,¼, -¼ | ¼,¼, -¼ | ¼,¼, -¼ | ¼,¼, -¼    |
| O        | -¼, -¼, -¼ | ¼,¼, -¼ | ¼,¼, -¼ | Vs       | Vs         |
| O        | -¼, -¼, -¼ | -¼, -¼, -¼ | -¼, -¼, -¼ | -¼, -¼, -¼ | -¼, -¼, -¼ |
| O        | -¼, -¼, -¼ | -¼, -¼, -¼ | -¼, -¼, -¼ | -¼, -¼, -¼ | -¼, -¼, -¼ |
| O        | -¼, -¼, -¼ | -¼, -¼, -¼ | -¼, -¼, -¼ | -¼, -¼, -¼ | -¼, -¼, -¼ |
| O        | -¼, -¼, -¼ | -¼, -¼, -¼ | -¼, -¼, -¼ | -¼, -¼, -¼ | -¼, -¼, -¼ |

The crystals Zr₄O₈, Zr₄O₇V, Zr₃MeO₇V, Zr₄O₅VsO and Zr₃MeO₆VsO are, of course, hypothetical with respect to both composition and structure. By definition they have the same lattice period equal to that for zirconia (a = 0.514777 nm) and, moreover, show an ordered arrangement of vacancies (in reality these may be distributed within their sublattice statistically).

The system is treated as a large molecule. The energy levels and wave functions for a cell are obtained with the help of molecular-orbital treatment. The obtained wave functions have precise physical interpretation in a sense of a degree of localization of a charge. We considered electronic properties calculated for a group of atoms of dioxide when one cation site is replaced with impurity atom and one anion is absent and the nearest neighbor atom O moved along the impurity to a vacant site.

**MOLECULAR-ORBITAL TREATMENT**

In the theory of SPD-bonded systems the electronic eigenstates are written in terms of a basis set consisting of a single S-state, five D-states of each metal atom, and three P-states on each oxygen atom of zirconia. The corresponding one-electron eigenvalues and eigenfunctions are then obtained by diagonalizing an NxN Hamiltonian matrix based upon these N orbitals. In the given work, the basis system of zirconia consisted of one 5S orbital and five 4D orbitals of zirconium and three 2P orbitals of oxygen atom of zirconia. We use parameters consisting of values for diagonal terms eₕ = -5.68 eV, e₃d = -8.46 eV, e₃p = -16.72eV.

For calculations of energy levels of cubic zirconia in the absence of a defect, we used a cell of 12 atoms, including 8 oxygen and 4 zirconium atoms, which are given above. The center of the cell was taken at the oxygen unit. For the oxygen vacancy, one simply...
removes the central atom of the cell. The nearest neighbor oxygen atom is displaced in
the direction of the central vacant unit, and then the calculations are repeated.

On different atoms these orbitals are assumed orthogonal. However, atomic orbitals are
not eigenfunctions of the considered quantum-mechanical system, as the Hamiltonian
matrix elements between orbitals of various atoms are not equal to zero; and we use, to
account for diagonal elements, the data (9,10) for energy of S- and D- states of 26 D-
elements. The matrix elements of SP- and PD-type were considered on the basis of the
pseudo-potential theory for transition metals (9).

To find the eigenfunctions and eigenvalues of the system energy, it is necessary to
diagonalize the symmetric matrix $H_{\mu\nu}$.

The single-electron orbitals of our cell can be expressed as

$$\Phi_\alpha = \sum_j^{N_Zr} \left( c_j^s |5s^j\rangle + \sum_{k=1}^5 c_4^j |4d^j_k\rangle \right) + \sum_{\omega=1}^{NO} \sum_{i=1}^{3} c_{p_i}^\omega |2p_i^j\rangle$$ \hspace{1cm} [1]

where $N_Zr$ is the number of zirconium atoms; $NO$ is the number of oxygen atoms; $i$ runs
along the value of the three coordinate axes; $c_\alpha$ is the solution of the one electronic
equation for a cell:

$$\sum_\nu \left( H_{\mu\nu} - \delta_{\mu\nu} E_\alpha \right) _{\nu\alpha} = 0, \hspace{1cm} \alpha = 1,2..,n$$ \hspace{1cm} [2]

where $E_\alpha$ is the single-electron eigenvalue of the cell energy and $H_{\mu\nu} = $ the matrix
elements between hybridized orbitals.

The wave function electron, located on impure d-element whose factors are the solution
of Eq. [2], is given as a sum composed of 5S- and 4D- orbitals of each zirconium atom,
2P-orbitals of each atom of oxygen, both ns- and (n-1) d-orbitals of the impurity atom.

$$\Phi_\alpha = \sum_j^{N_Zr} \left( c_j^s |5s^j\rangle + \sum_{k=1}^5 c_4^j |4d^j_k\rangle \right) + \sum_{\omega=1}^{NO} \sum_{i=1}^{3} c_{p_i}^\omega |2p_i^j\rangle +$$

$$+ c_{3s}^{Me} |ns\rangle + \sum_{\omega=1}^{s} c_{ns}^{Me} |(n-1)d_\omega\rangle$$ \hspace{1cm} [3]

where

$N_Zr$ is the number of zirconium atoms
$NO$ is the number of oxygen atoms
$NH$ is the number of hydrogen atoms
$i$ runs along the value of the three coordinate axes
$c_\alpha$ solution of the one-electronic equations for a cell.

We now describe the results of the calculation.
RESULTS AND DISCUSSION

The band structure of ZrC\textsubscript{2} has a forbidden gap. The filled band consists of both connected orbitals Zr and O and orbitals located only on atoms of oxygen. The atomic p-level of oxygen keeps the state as well as the d-level of zirconium in a free band. Thus electrons from d-levels pass on p-levels of oxygen, providing the ionic character.

As described in (11), a measure of the total energy of the system is given by the sum of the energies of all the occupied one-electron molecular orbitals. That is,

$$E_{\text{tot}} = \sum n_i \varepsilon_i,$$  \hspace{1cm} [4]

where $\varepsilon_i$ is the energy and $n_i$ the occupation number of the $i$-th orbital. A rough estimate of the migration energy for the vacancy can be obtained by monitoring the total energy of the cell as was done in (11).

Our calculations have shown that the oxygen vacancy in zirconia is split vacancy. We define a migration barrier in undoped zirconia as approximately 0.8 $E_g$. The one-electronic molecular-orbital energy was received when one cation site of a cell was replaced by d-impurity. The orbitals, connected with Y, Zr, Lu, and Hf, are absent in the forbidden gap of zirconia. The orbitals, connected with Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, Te, Ru, Rh, Pd, Ag, Ta, W, Re, Os, Ir, Pt, and Au appear in the forbidden gap.

A rough estimate of the migration barrier for oxygen in doped zirconia can be obtained by monitoring the sum of the energies of all the occupied one-electron molecular orbitals of the cell at moving oxygen. The results of calculations of influence 26 d-dopants on the migration barrier are submitted in Figure 1. We have established that the migration barrier for oxygen in zirconia sharply decreases with Cu, Ag, Ni, Pd, Pt and Au doping.

Figure 1. Relation between migration barrier for oxygen in pure zirconia and with 26 d-dopants.
REFERENCES

1. S. Primdahl, B. F. Sorensen, and M. Mogensen, *J. Am. Ceram. Soc.*, **83** 489-494 (2000).

2. H. Matzke. CIMTEC 98, Florence, Italy, 14-19 June 1998, Abstracts, p. 216.

3. V. V. Tokiy, N. V. Tokiy, T. E. Konstantinova, and V. N. Varyuhin, British Ceramic Proceedings No.60, The Sixth Conference and Exhibition of the European Ceramic Society, *Vol. 2*, pp. 491-492 (1999).

4. V. Tokiy, D. Savina, N. Tokiy, T. Konstantinova, and V. Varyuhin, 9th Cimtec-World Forum on New Materials, Symposium IV, Diamond Films, Editor P. Vincenzini, pp.193-200 (1999).

5. N. V. Tokiy, D. L. Savina, and T. Y. Konstantinova, 4th High Pressure School on Chemistry, Biology, Materials Science and Techniques, Warsaw (2001).

6. T. Y. Konstantinova, N. V. Tokiy, and D. L. Savina, CERAM-2001, Kiev, p. 56 (2001).

7. N. Tokiy, T. Konstantinova, D. Savina, and V. Tokiy, SI-IV. CIMTEC 2002, Florence (2002).

8. T. Konstantinova, I. Danilenko, A. Dobrikov, G. Volkova, V. Tokiy, and S. Gorban, A:P07, CIMTEC’2002, Florence (2002).

9. W. A. Harrison, *Electronic Structure and the Properties of Solids*, Freeman, San Francisco, 1980, reprinted by Dover, New York (1989).

10. W. A. Harrison, *Phys. Rev. B*, **41**, p. 6008-6019 (1990).

11. N. Tokiy, V. N. Varyuhin, and V. V. Tokiy, Proceedings of 4th international symposium on diamond films and related materials, p. 99-102 (1999).