Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

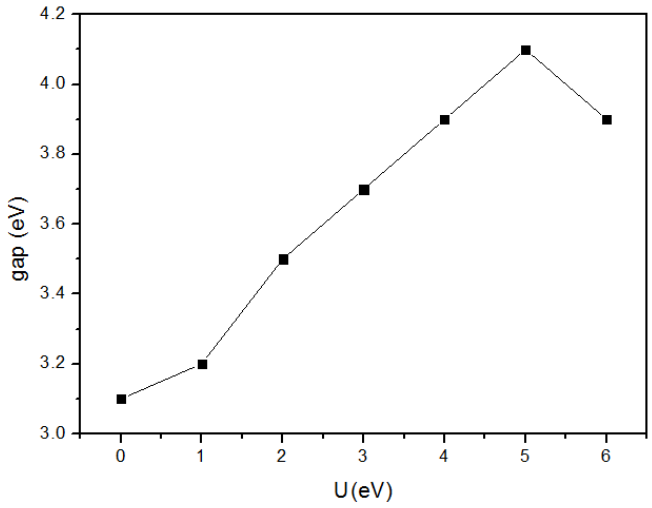
The mechanisms for the high resistance to sulfur poisoning of the Ni/Yttria-Stabilized Zirconia system treated with Sn vapor

Yanxing Zhang, Zhaoming Fu, Shan Dong, Zongxian Yang*

College of Physics and Electronic Engineering, Henan Normal University, Xinxiang, Henan 453007, People's Republic of China

1. The details of DFT+U tests

In order to study the effect of the strong electron correlation of Zr and Y, we made test calculations using the DFT+U method[1], where the parameter U is equivalent to the U_{eff} (=U - J). We first test the U value of the Zr element in the c-ZrO_2 structure. The U dependent band gap is shown below. The predicted band gap of c-ZrO_2 is 3.1 eV with U=0, which is smaller than the experimental values (5.4, 5.7 eV)[2, 9], but agrees with other first-principle studies[3-5]. It is shown that the band gap has the biggest value when U=5, so we will select the U = 5 eV for further test. For the cubic Y_2O_3, the calculated bond gap is 4.1 eV with U = 0 eV, which agrees with other first-principle studies[6] and is smaller than the experimental value[7] of 6 eV. Our tests with different U values for Y in the cubic Y_2O_3 structure show that the band gap tends to be reduced with the addition of U. For example, even with a small value of U (e.g., 1 eV), the calculated band gap decreases to 4.0 eV. So we choose a U = 0 eV for Y for further test.



* Author to whom correspondence should be addressed.
Electronic mail: yzx@henannu.edu.cn (Z Yang)

So we make test using the U values of 5 eV for Zr and 0 eV for Y to check the influence due to strong electron correlation. We calculate the S adsorption energies on the NiSn-d/YSZ and NiSn-d/YSZ-Ov systems. It is found that for the case of NiSn-d/YSZ, the S adsorption energies have no change at all the sites, while for the case of NiSn-d/YSZ-Ov, the S adsorption energies only increase a little (about 0.1 eV), which is about 2% of the original values. It is therefore expected that the strong electron correlation does not have significant influence on our results. Therefore, in the calculations, we do not take into consideration the strong electron correlation of the d electrons of Zr and Y.

1. S. Dudarev, G. Botton, S. Savrasov, C. Humphreys and A. Sutton, *Phys. Rev. B*, 1998, **57**, 1505-1509.
2. S. Sayan, R. Bartynski, X. Zhao, E. Gusev, D. Vanderbilt, M. Croft, M. Banaszak Holl and E. Garfunkel, *physica status solidi (b)*, 2004, **241**, 2246-2252.
3. O. I. Malyi, P. Wu, V. V. Kulish, K. Bai and Z. Chen, *Solid State Ionics*, 2012, **212**, 117-122.
4. C. Århammar, C. M. Araújo and R. Ahuja, *Phys. Rev. B*, 2009, **80**, 115208.
5. J. Čížek, O. Melikhova, I. Procházka, J. Kuriplach, R. Kužel, G. Brauer, W. Anwand, T. E. Konstantinova and I. A. Danilenko, *Phys. Rev. B*, 2010, **81**, 024116.
6. J. Zheng, G. Ceder, T. Maxisch, W. K. Chim and W. K. Choi, *Phys. Rev. B*, 2006, **73**, 104101.
7. J. Robertson, *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures*, 2000, **18**, 1785-1791.

2. The structure (.cif format) of the triple phase boundary (TPB) Ni/YSZ model

Cell length a	12.5659 Å
Cell length b	7.25492 Å
Cell length c	22.4045 Å
Cell angle alpha	90 degree
Cell angle beta	90 degree
Cell angle gamma	90 degree

Fractional coordinates

O1	O	0.22343130	0.28661010	0.33089105
O2	O	0.72860003	0.29506934	0.31166182
O3	O	0.43772072	0.98467982	0.35636757
O4	O	0.95452958	0.98463684	0.35561758
O5	O	0.43515733	0.49410009	0.33152626
O6	O	0.95503658	0.48592708	0.33458872
O7	O	0.22309522	0.69591635	0.32817790
O8	O	0.72596580	0.68148553	0.31108350
O9	O	0.04052075	0.74455637	0.26895250
O10	O	0.53306246	0.74744105	0.26407706
O11	O	0.04305528	0.22726719	0.27145808

O12	O	0.53874207	0.22225457	0.27295199
O13	O	0.30578643	0.99726784	0.26493051
O14	O	0.81511265	0.98364961	0.26562746
O15	O	0.14035252	0.49396846	0.20776984
O16	O	0.63877290	0.49514255	0.20299126
O17	O	0.13222037	0.96768701	0.19949763
O18	O	0.63740796	0.97655070	0.19892752
O19	O	0.35209921	0.70992750	0.20953112
O20	O	0.87430638	0.69455707	0.20765158
O21	O	0.36709654	0.29470775	0.21506807
O22	O	0.86536038	0.26247197	0.20633769
O23	O	0.46039787	0.50011885	0.13012647
O24	O	0.96266752	0.49197710	0.12892129
O25	O	0.20777708	0.73084933	0.12779593
O26	O	0.71247935	0.73768771	0.12890444
O27	O	0.45315722	0.96928787	0.13758766
O28	O	0.95420396	0.96970898	0.13554058
O29	O	0.21974532	0.22831763	0.13056542
O30	O	0.71580619	0.23354810	0.12860996
O31	O	0.04444443	0.73333329	0.06609843
O32	O	0.54444444	0.73333329	0.06609843
O33	O	0.29444444	0.48333332	0.06609843
O34	O	0.79444444	0.48333332	0.06609843
O35	O	0.29444444	0.98333329	0.06609843
O36	O	0.79444444	0.98333329	0.06609843
O37	O	0.04444443	0.23333330	0.06609843
O38	O	0.54444444	0.23333330	0.06609843
O39	O	0.12777777	0.98333329	-0.00000000
O40	O	0.62777776	0.98333329	-0.00000000
O41	O	0.37777776	0.73333329	-0.00000000
O42	O	0.87777776	0.73333329	-0.00000000
O43	O	0.37777776	0.23333330	-0.00000000
O44	O	0.87777776	0.23333330	-0.00000000
O45	O	0.12777777	0.48333332	-0.00000000
O46	O	0.62777776	0.48333332	-0.00000000
Zr47	Zr	0.11709662	0.48671404	0.29931145
Zr48	Zr	0.60304880	0.48792651	0.29717798
Zr49	Zr	0.38000715	0.22582737	0.30609058
Zr50	Zr	0.88753015	0.21764235	0.30430837
Zr51	Zr	0.37855238	0.75854707	0.30217078
Zr52	Zr	0.88720816	0.75071239	0.30458287
Zr53	Zr	0.28664348	0.96441025	0.16323637
Zr54	Zr	0.79096222	0.99869627	0.16412674
Zr55	Zr	0.29536203	0.48339701	0.15939506

Zr56	Zr	0.79641414	0.48497048	0.15909405
Zr57	Zr	0.03838487	0.73389477	0.16675837
Zr58	Zr	0.55296409	0.73708493	0.16413808
Zr59	Zr	0.46111110	0.98333329	0.03304922
Zr60	Zr	0.96111113	0.98333329	0.03304922
Zr61	Zr	0.46111110	0.48333332	0.03304922
Zr62	Zr	0.96111113	0.48333332	0.03304922
Zr63	Zr	0.21111110	0.73333329	0.03304922
Zr64	Zr	0.71111113	0.73333329	0.03304922
Zr65	Zr	0.21111110	0.23333330	0.03304922
Zr66	Zr	0.71111113	0.23333330	0.03304922
Y67	Y	0.13884920	0.98447388	0.30067932
Y68	Y	0.64327800	0.98313642	0.30097464
Y69	Y	0.04591907	0.23287897	0.16745736
Y70	Y	0.54015672	0.23627263	0.16875897
Ni71	Ni	0.52352196	0.48979765	0.40650023
Ni72	Ni	0.52815574	0.15173259	0.41206836
Ni73	Ni	0.52786851	0.82793009	0.41093149
Ni74	Ni	0.60392570	0.32541695	0.48903870
Ni75	Ni	0.70292187	0.66657609	0.39757751
Ni76	Ni	0.79337257	0.32605463	0.49528039
Ni77	Ni	0.70351076	0.31055400	0.39790052
Ni78	Ni	0.70042324	0.98624593	0.44149132
Ni79	Ni	0.79342824	0.65748686	0.49491928
Ni80	Ni	0.56235069	0.99157852	0.50792867
Ni81	Ni	0.60403836	0.65823263	0.48889067
Ni82	Ni	0.69088477	0.49187720	0.56808779
Ni83	Ni	0.87341660	0.48980084	0.41147281
Ni84	Ni	0.87608069	0.83050001	0.42170460
Ni85	Ni	0.68984085	0.15693712	0.56607640
Ni86	Ni	0.68979913	0.82679218	0.56596662
Ni87	Ni	0.82706916	0.99105060	0.51680157
Ni88	Ni	0.87499219	0.14972346	0.42238655