MODEL OF CONDUCTIVITY IN DOPED SnO_2–BASE INERT ANODES FOR Al–ELECTROWINNING①

Yin, Zhoulan Yang, Jianhong Wang, Huazhang
Zhao, Qinsheng Liu, Yexiang Gao, Xiaohui
Central South University of Technology, Changsha 410083, China

ABSTRACT

The variations of chemical bonding characteristics in doped SnO_2-base inert anodes with various dopants are studied using CNDO / 2 quantum chemical calculations. A new model of conductivity is derived,which is checked with literature data and our experimental results. Proper dopants can be selected with the model to reduce the resistivity of said electrode effectively.

Key words: doped SnO_2-base inert anodes quantum chemistry conductivity dopants

1 INTRODUCTION

Since the SnO_2-base inert anode was applied to the electrowinning process of aluminum from the cryolite–Al_2O_3 molten salts in 1930s, much work has been done about the conductivity of the anode and how to raise it by doping. Xue *et al*[1] adopted the 2–probe method to detect the resistivity of the anode and found that its conductivity can be raised by controlling the valence of the dopant or promoting the sintering process of the anode when it is doped by Sb_2O_3, CuO or ZnO. Wang *et al*[2] studied the effect of the six dopants of Sb_2O_3, CuO, ZnO, MnO_2, Fe_2O_3 and Cr_2O_3 on the physical properties of the anode such as the resistivity with plural progressive regression. In this paper, the variations of the chemical bonding characteristics in doped SnO_2-base inert anodes are studied with CNDO / 2 quantum chemical calculations. By investigating the mechanism of the conduction of electricity in the doped anodes, a new model of conductivity is derived, which is checked with literature data and our experimental results. Proper dopants can be selected with the model to reduce effectively the resistivity of the anodes.

2 QUANTUM CHEMICAL CALCULATIONS

2.1 *Calculation Method*

CNDO / 2 calculations are adopted which are well applicable for the comparison of the electric or magnetic properties in homologues. The program is run on a Siemens 7570C computer with the necessary atomic parameters from Pople *et al*[3].

A SnO_2 unit cell with 15 atoms and 24

① Manuscript received February, 17, 1992

net charges shown in Fig.1 is taken as the calculation model of the SnO_2-base. All the atoms in the model are numbered from 1 to 15. In order to examine the effect of every dopant on the bonding characteristics of the SnO_2 unit cell, Sn^{4+} is replaced by a metallic cation of the dopant. As is known[4], many metallic cations are almost the same in radii as Sn^{4+} and often take the place of Sn^{4+} in natural tinstone in isomorphous form. Therefore, we can choose such cations as Sb^{3+}, Cu^{2+}, Zn^{2+}, Mn^{4+}, Cr^{3+}, Ni^{2+}, Ti^{4+}, V^{5+}, Co^{3+}, Y^{3+}, Zr^{4+}, Nb^{5+}, $Bi^{5+}$and Ir^{4+}, the radii of which are almost the same as that of Sn^{4+}[5], to replace Sn^{4+} in our calculations. The corresponding dopants of oxide are Sb_2O_3, CuO, ZnO, MnO_2, Fe_2O_3, Cr_2O_3, NiO, TiO_2,V_2O_5, Co_2O_3, Y_2O_3, ZrO_2, Nb_2O_5, Bi_2O_5 and IrO_2. The Sn^{4+} to be replaced is selected from the centre of the unit cell so that the calculation results are symmetrical. It is supposed that the lattice parameters of the SnO_2 unit cell remain constant after the replacement of Sn^{4+} by the cations. The necessary lattice parameters of SnO_2 for counting the coordinated of every atom are taken from Samsonov[6].

2. 2 *Calculation Results*

The compositions of the highest occupied molecular orbitals (HOMO) of SnO_2 and doped SnO_2 unit cells are obtained with CNDO / 2 calculations. The atoms are classified as shown in Table 1, where the numbers refer to those of the numbered atoms and where oxides (except SnO_2) refer to the dopants in SnO_2 unit cell. The atoms that participate in the formation of HOMO are marked as ✓.

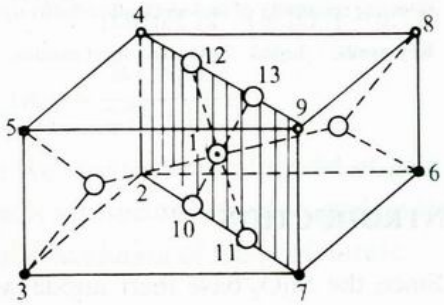

Fig. 1 The whole unit cell of SnO_2

●—Sn^{4+} ○—O^{2-} ⊙—Sn^{4+}or doped ion

Table 1 Atoms participating in HOMO formation of SnO_2 and SnO_2 unit cells

	SnO_2	Sb_2O_3	CuO	ZnO	MnO_2	Fe_2O_3	Cr_2O_3	NiO	TiO_2	V_2O_3	Co_2O_3	Y_2O_3	ZrO_2	Nb_2O_5	Bi_2O_5	IrO_2
1	✓		✓		✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓
2		✓		✓	✓	✓	✓		✓	✓		✓	✓	✓		
3			✓			✓	✓			✓	✓	✓	✓	✓		
4		✓		✓	✓	✓	✓		✓	✓		✓	✓	✓		
5			✓			✓	✓			✓	✓	✓	✓	✓		
6			✓			✓	✓			✓	✓	✓	✓	✓		
7		✓		✓	✓	✓	✓		✓	✓		✓	✓	✓		
8			✓			✓	✓			✓	✓	✓	✓	✓		
9		✓		✓	✓	✓	✓		✓	✓		✓	✓	✓		
10	✓	✓	✓	✓	✓	✓		✓	✓	✓			✓	✓	✓	
11	✓	✓	✓	✓	✓	✓		✓	✓	✓			✓	✓	✓	
12	✓	✓	✓	✓	✓	✓		✓	✓	✓			✓	✓	✓	
13	✓	✓	✓	✓	✓	✓		✓	✓	✓			✓	✓	✓	
14	✓		✓			✓	✓	✓		✓	✓	✓			✓	✓
15	✓		✓			✓	✓	✓		✓	✓	✓			✓	✓

3 THE MODEL OF CONDUCTIVITY

SnO_2 and doped SnO_2–base anodes are semiconductors in which the simulated electrons in HOMO conduct electricity. Therefore only the atoms which participate in the formation of HOMO supply the electrons to form electricity. In SnO_2 anode, the atoms which participate in the formation of HOMO and supply the electrons to form electricity are those numbered 1, 10, 11, 12, 13, 14, 15 and situated in all three dimensions. As a result, the resistance of the lattice to the flow of electrons to form electricity is large, i. e. the resistivity of the anode is large and its conductivity small.

When the SnO_2-base is doped by Sb_2O_3, the atoms which participate in the formation of HOMO and supply the electrons to form electricity change to those numbered 2, 4, 7, 9, 10, 11, 12, 13. They are located on one plane which is depicted by the shaded area in Fig. 1. The resistance of the lattice to the flow of the electrons on the plane to form electricity becomes smaller and thus the resistivity of this doped SnO_2–base anode is reduced and its conductivity raised. Such dopants as ZnO, MnO_2, TiO_2, Co_2O_3 and IrO_2 have the same function as Sb_2O_3. Conductivity of the SnO_2-base anode with any of these dopants will be raised.

When the SnO_2-base is doped by Fe_2O_3, the atoms which supply the electrons to form electricity change to 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 and 15. That is , all the atoms in the lattice participate in the formation of HOMO. They are situated in all three dimensions rather than on one plane. The resistance of the lattice to the flow of electrons to form electricity is increased. Therefore the addition of Fe_2O_3 to the SnO_2-base anode will reduce the conductivity of the anode. Such dopants as CuO, Cr_2O_3, NiO, V_2O_5, Y_2O_3, ZrO_2, Nb_2O_5 and Bi_2O_5 have the same function as Fe_2O_3. The atoms participating in the formation of HOMO in the SnO_2-base anode doped by any of above dopants are situated in all three dimensions.

Only one Sn^{4+} in the centre of the SnO_2 unit cell is replaced by a cation of dopant in our CNDO / 2 calculations. Therefore the above-mentioned new model of conductivity is applicable only for the doped SnO_2-base anodes with the model at a too high or too low concentrations. In addition, as the results of quantum chemical calculations reveal, in theory, the bonding characteristics at the temperature of absolute zero, any difference in the conductivity of the anode caused by the variation of its physical or chemical properties with increasing temperature is neglected in the model.

4 VERIFICATION OF THE MODEL

From the new model of conductivity, it is known that atoms participating in the formation of HOMO are located on one plane if the SnO_2-base anode is doped by Sb_2O_3, ZnO, TiO_2, Co_2O_3 or IrO_2. The electrons in them are easily stimulated and flow on the plane to form electricity. The resistance of the lattice to the flow of the electrons to form electricity is decreased. So the resistivity of any of these doped SnO_2-base anode is reduced and its conductivity raised. If the SnO_2-base anode is doped by Fe_2O_3, CuO, Cr_2O_3, NiO, V_2O_5, Y_2O_3, ZrO_2, Nb_2O_5 or Bi_2O_5, atoms participating in the formation of HOMO are situated in all three dimensions. The resistance of the lattice to the flow of the electrons supplied by

these atoms to form electricity is increased. The resistivity of any of these doped SnO_2-base anodes is raised and its conductivity reduced. The above prediction of the variation of conductivity is checked with literature data and our experiments as follows.

4.1 *The Experimental Conditions*

SnO_2 and doped SnO_2-base anodes were prepared by powder sintering[7]. SnO_2 and all the dopants of oxide were reagent grade. The anodes were pressed and shaped before sintered at 1,350℃ in air for 5 h.They were cylindrical with a length to diameter ratio greater than 3. All the anodes were prepared in one batch with the same technique to make sure that they were comparable. A four-probe method was adopted to measure the conductivities of the anodes in view of the stabilities of semiconductors[7].

4.2 *The Experimental Results*

SnO_2-base anodes doped by TiO_2, V_2O_5, Co_2O_3, Y_2O_3, Bi_2O_5 and Nb_2O_5 were prepared. Their conductivities together with some of their physical properties were measured as shown in Table 2. All of them were the average values of more than 2 measurements. The amounts of the dopants in SnO_2 were 1～3 wt-%.

Table 2 shows that the conductivity of the SnO_2-base anode doped by TiO_2 or Co_2O_3 is greatly raised while that of the SnO_2-base anode doped by V_2O_5 or Y_2O_3 is reduced, which coincides with the model. The conductivity of Bi_2O_5 or Nb_2O_5 doped SnO_2-base anode is slightly increased, which seems to contradict with the model. But as is known[8], Bi_2O_5 and Nb_2O_5 easily lose their oxygen at high temperatures to become nonstoichiometric with their conductivities raised. By comparing the increase of the conductivities in a Bi_2O_5 or Nb_2O_5 doped and a TiO_2 or Co_2O_3 doped SnO_2-base anodes, we notice that the conductivity of a Bi_2O_5 or Nb_2O_5 doped SnO_2-base anode is not raised greatly even though there exist defects and the nonstoichiometry of oxygen in Bi_2O_5 and Nb_2O_5.

The variations of conductivity in doped SnO_2-base anodes predicted from the new model are listed in Table 3 with the literature data and our experimental results. Table 3 indicates that the literature data and our experimental results coincide well with the predicted conductivities, which supports the model very well. In addition, the conductivity of the SnO_2-base anode doped by CuO is reduced at low temperatures. This is identical with the prediction of the model. But the physical and chemical properties of CuO vary at high temperatures because of the formation of the CuO–Cu_2O liquid phase which can wet the SnO_2

Table 2 The conductivities of doped SnO_2–base inert anodes

No.	component	density / g.cm^{-3}	porosity / %	conductivity / $\times 10^{-4}\Omega^{-1}$cm^{-1}				
				600 / ℃	700 / ℃	800 / ℃	900 / ℃	970 / ℃
028SA01	SnO_2	4.083	41.77			0.509	3.401	13.24
038SA01	SnO_2–TiO_2	4.252	39.10	16.6	127	590	1231	1536
036SA01	SnO_2–V_2O_5	5.286	22.96			1.822	3.081	6.027
025SA01	SnO_2–Co_2O_3	5.266	24.96	531	2451	4161	5958	7181
032SA01	SnO_2–Y_2O_3	4.539	37.34			0.483	2.857	8.14
039SA01	SnO_2–Bi_2O_5	6.822	0.052			6.812	20.07	37.49
030SA02	SnO_2–Nb_2O_5	5.120	26.04		7.474	29.50	93.43	

crystalline grain to reduce greatly the porosity of the anode and enhance the contact between the crystalline grains to reduce the contact resistance. As a result of that, the sintering process is promoted and the conductivity of the anode is raised at high temperatures.

Table 3 The predicated (p.) and experimental (e.) conductivities of doped SnO_2–base inert anodes*

dopant	Sb_2O_3	CuO	ZnO	MnO_2	Fe_2O_3	Cr_2O_3	NiO
p.	↑	↓	↑	↑	↓	↓	↓
e.	↑ [1.2]	↓ [1.2]*	↑ [1.2]	↑ [1]	↓ [1.2]	↓ [1]	↓ [2]
	TiO_2	V_2O_3	Co_2O_3	Y_2O_3	ZrO_2	Nb_2O_5	Bi_2O_5	IrO_2
	↑	↓	↑	↓	↓	↓	↓	↑
	↑ [author]	↓ [author]	↑ [author]	↓ [author]		↓ [author]	↓ [author]	

* ——at low temperature ; ↑ ——raise ; ↓ ——reduction ; [ ]——references

The effect of the remaining of the dopants in Table 3 on the conductivities of the SnO_2-base anodes needs to be checked further due to the lack of chemical reagents.

From the above discussion, it is known that the conductivity of any binary doped SnO_2-base anode can be predicted correctly with CNDO / 2 calculations of quantum chemistry and the new model of conductivity, which provides a convenient way to select proper dopants of oxide to raise the conductivity of the SnO_2-base inert anode.

5 CONCLUSIONS

With the quantum chemical calculations for SnO_2 and doped SnO_2 unit cells, a new model of conductivity in the doped SnO_2-base inert anode for the electrowinning of aluminum is derived by analysing the compositions of frontier molecular orbitals. It is proposed that the conductivity of the SnO_2–base inert anode doped by Sb_2O_3, ZnO, MnO_2, TiO_2, Co_2O_3 or IrO_2 is raised. Most of the predictions about the effect of the dopants on the conductivities of the anodes are checked with literature data and our experimental results.

REFERENCES

1 Xu,e J. L. *et al.* J of North East University of Technology, 1990, 11(4): 362.

2 Wang, H. Z. *et al.* Ganshu Nonferrous Metallurgy, 1989, 3: 63.

3 Pople, J. A. *et al*, Approximate Molecular Orbital Theory, McGrawe–Hill, 1970.

4 Research Section of Minerals of Wuhan Institute of Geology. Crystallography and Mineralogy, Vol. 2, Geology Press, 1970.

5 Plane, R. A. *et al*(ed). Physical Inorganic Chemistry. Benjamin, W. A. Inc, 1963.

6 Samsonov, G. V. The Oxide Handbook, 2nd. IFI / Plenum Data Company, 1982.

7 Yang, J. H. Doctral Thesis of the Central–South University of Technology, 1992.

8 Rao, C. N. *et al.* New Directions in Solid State Chemistry: Structure, Synthesis, Properties, Reactivity and Materials Design. Cambridge University Press, 1986.