The nature of phase separation in Ir–Sn–O ternary oxide electrocatalyst

Xin Wang a, Qianqian Yin a, Zhongzhi Tang b, Xuehua Liu b, Dian Tang a,b,∗∗, Wei Lin b,∗,1

a College of Material Science and Engineering, Fuzhou University, Fuzhou, Fujian, 350108, China
b Institute of Materials Research, Fuzhou University, Fuzhou, Fujian, 350108, China
Received 22 April 2013; received in revised form 20 June 2013; accepted 1 July 2013

Abstract

Phase diagram of iridium-tin oxide (Ir–Sn–O) was calculated by a combination of ab initio density functional theory (DFT) and thermodynamic calculations. Results suggested that the phase separation that had been reported in literature for Ir–Sn–O was through a typical spinodal decomposition mechanism. Ir0.534Sn0.466O2 was prepared by a thermal co-decomposition method at 320 and 450 °C. Quantitative phase analysis based on DFT, X-ray diffraction and high-resolution transmission electron microscopy confirmed the spinodal nature of the phase separation. The present fundamental study is an important reference for phase and microstructure design of Ir–Sn–O for various electrocatalysis applications. The DFT-assisted quantitative phase analysis has provided peer researchers with a novel reliable phase analysis approach for complex compounds.

© 2013 Elsevier Ltd. All rights reserved.

Keywords: Iridium tin oxide; Ab initio; Density functional theory; Phase diagram; Quantitative phase analysis

1. Introduction

Iridium oxide (Ir2O3) and its complex oxides (in particular iridium–tin–oxide, Ir–Sn–O) are an important class of complex metal oxide for water electrolysis, oxygen and chlorine evolutions, and supercapacitor application, etc.1–15 From microstructure point of view, like many other complex oxides,16 true solid solution (Ir1−x,Snx)O2 (designated as a general formula for solid–solution Ir–Sn–O) is highly desired17 because of the higher electro-activity of an atomic level fine mixture than its counterpart of oxide mixtures as the products of phase separation.18 Albeit the extensive research interest in Ir–Sn–O, literature reports on possible formation of true solid solution (Ir1−x,Snx)O2 are widely scattered and controversial. Fundamental understanding of the stability of (Ir1−x,Snx)O2 is important for microstructure control and electro-activity optimization for the ternary metal oxide system, but is still lacking. We know that Ir–Sn–O conforms to almost all the Hume–Rothery rules for the formation of a substitutional solid solution phase: (1) Ir2O3 and SnO2 have the same rutile crystal structure at regular synthesis temperature (<600 °C); (2) Ir and Sn cations have the same valence state; (3) the size difference between the two cations (0.63 vs. 0.69 Å) is small;19 and (4) the electronegativities of Ir and Sn are close (1.94 vs. 1.73).19 Therefore, formation of unlimited (Ir1−x,Snx)O2 solid solution is expected.20 This lays an semi-empirical explanation for the stability of (Ir1−x,Snx)O2 reported in literature.6,11–13 However, phase separations and very low solubility have also been reported frequently for Ir–Sn–O.7,10,11,21,22 Although these experiments all provided certain inputs to qualitative understanding of the phase stability of Ir–Sn–O, the very conflicting results in literature suggest the need for a mechanistic analysis of the phase stability/separation of (Ir1−x,Snx)O2 solid solution. Moreover, a reliable quantitative phase analysis has rarely been reported. In the present study, we use a combined ab initio density functional theory (DFT) and thermodynamic modelling to construct binodal and spinodal diagrams for Ir–Sn–O, with the intent to provide fundamental explanations for the reported phase behaviours of this oxide system. By combining DFT calculation, elemental analysis, and X-ray diffraction, we demonstrate a general quantitative phase analysis approach that
can be applied to various multi-component compound/mixture systems.

2. Calculation and experimental

2.1. Thermodynamic method

A single-phase ternary Ir–Sn–O oxide can be treated as a quasi-binary compound composed of IrO2 and SnO2.23–25 The formation of (Ir1−xSn)xO2 solid solution from its virtual composition oxides, IrO2 and SnO2 of the same crystal structure (rutile in this case), can be expressed by Eq. (1):

\[(1 - x)\text{IrO}_2 + x\text{SnO}_2 = (\text{Ir}_{1-x}\text{Sn}_x)\text{O}_2\] (1)

Choosing one atmosphere as the pressure condition for the standard state, the Gibbs free energy of the (Ir1−xSn)xO2 phase at a temperature \(T\) is given by Eq. (2):

\[G(T) = (1 - x)^0G_{\text{IrO}_2}(T) + x^0G_{\text{SnO}_2}(T) + x(1 - x)\Omega + RT [\ln(1 - x) + x \ln x]\] (2)

where the \(G_{\text{IrO}_2}(T)\) and \(G_{\text{SnO}_2}(T)\) are the standard Gibbs free energies of the compositional oxide phases in their stable states at temperature \(T\). Thus, the Gibbs free energy of mixing \((G^m)\) is given by Eq. (3):

\[G^m = x(1 - x)\Omega + RT [(1 - x)\ln(1 - x) + x \ln x]\] (3)

where the second term is the temperature-dependent configurational entropy. The first term is the enthalpy of mixing, \(H^m\), where \(\Omega\) is the interaction parameter reflecting the enthalpy change by mixing the oxides. In the present study, to account for the dependence of \(H^m\) on the temperature and composition \(x\), we consider \(\Omega\) a function of \(T\) and \(x\). Taking \(\Omega\) as a function of \(T\) and \(x\) is a widely used method in literature for inorganic compounds.24,25

2.2. Ab initio DFT calculations

\(H^m\) at 0 K can be obtained by \textit{ab initio} DFT calculations. The \textit{ab initio} calculations were carried out using the Vienna \textit{Ab initio} Simulation Package (VASP). The details of calculations have been described in our recent publication.24,25 Briefly, Local Density Approximation (LDA) was chosen. \(K\) points of \(6 \times 6 \times 6\) (Monkhorst–Pack grid) determined according to the Monkhorst–Pack scheme was used for the integration in Brillouin zone. The unit cell volume \(V\) was calculated using the self-consistent wave function at 0 K for different lattice values until the convergence in the total energy was lower than \(2 \times 10^{-5}\) eV per metal atom of a 24-atom supercell. In the calculations, Ir and Sn atoms were distributed randomly within the metal sublattice.

To determine the equilibrium unit cell volume \(V_0\), the total energy \((E)\) was calculated as a function of the volume by means of \textit{ab initio} DFT. Murnaghan equation of state, Eq. (4),26 was then applied to fit the calculated \(E-V\) curve to obtain \(V_0\), the bulk modulus \((B_0)\), and the equilibrium total energy \(E_0\) for \((\text{Ir}_{1-x}\text{Sn}_x)\text{O}_2\) with a varied \text{SnO}_2 fraction.

\[E_{\text{Murn}}(V) = -E_0 + \frac{B_0V}{B_0'} \left(\frac{V_0}{V}\right)^{B_0'} + \frac{B_0V_0}{B_0'} \left(1 - \frac{V_0}{V}\right)^{B_0'} - B_0V_0 \left(\frac{V_0}{V}\right)^{B_0'} + \frac{B_0V_0}{B_0'} \left(1 - \frac{V_0}{V}\right)^{B_0'}\] (4)

For each preset value of \(x\), the enthalpy of formation of \((\text{Ir}_{1-x}\text{Sn}_x)\text{O}_2\) with a supercell containing 24 atoms was obtained by considering the following reaction:

\[8(1 - x)\text{Ir(solid)} + 8x\text{Sn(solid)} + 8O_2(gas) = 8(\text{Ir}_{1-x}\text{Sn}_x)\text{O}_2(\text{solid})\] (5)

Thus,

\[\Delta H_{f,(\text{Ir}_{1-x}\text{Sn}_x)\text{O}_2} = E_0,(\text{Ir}_{1-x}\text{Sn}_x)\text{O}_2 - xE_{0,\text{Sn}} - (1 - x)E_{0,\text{Ir}} - E_{0,\text{O}_2}\] (6)

The enthalpy of mixing is defined as:

\[H^m = \Delta H_{f,(\text{Ir}_{1-x}\text{Sn}_x)\text{O}_2} - x\Delta H_{f,\text{SnO}_2} - (1 - x)\Delta H_{f,\text{IrO}_2}\] (7)

2.3. Sample preparation and characterization

IrO2–SnO2 oxide coatings were prepared on commercial titanium (TA2) plates by a conventional industry-scale thermal decomposition method.27,28 Briefly, the Ti substrates (40 mm × 50 mm × 2 mm) were first etched in a 20 wt% concentrated sulfuric acid at 80°C for 1 h, washed thoroughly with distilled water, and then dried. 8.32 × 10⁻⁵ mol IrCl3·nH2O (35 wt% Ir) and 1.25 × 10⁻⁴ mol SnCl4·5H2O were dissolved separately in 0.55 mL and 0.65 mL anhydrous ethanol, respectively, and then mixed to form a precursor mixture. The precursor mixture was painted onto the substrate, dried by infrared light and thermally decomposed in air at 320°C for 10 min. The painting, drying, and decomposition were repetitively applied on the substrate for 20 times until all the precursors were coated on the substrate. The final Ir loading in the coating was 0.8 mg cm⁻². The as-prepared sample is designated as ISO320 from hereafter. A control sample (ISO450) was prepared via the same procedure except that the annealing duration was conducted at 450°C for 120 min as used in many references. Pure IrO2 and SnO2 coatings were also prepared via the same procedure at the same decomposition temperature with the control sample. Phase analyses of the oxide coatings were carried out using an X-ray diffractometer (XRD, Rigaku D/max-IIIc), with a copper Kα source (λ = 1.5406 Å) at the accelerating voltage of 35 kV and the current of 20 mA. The scanning rate of 2 degrees per minute with the step length of 0.02 degrees was used. High resolution transmission electron microscopy (HRTEM) was performed in a Tecnai G2 F20 S-TWIN Electron Microscope system at 200 kV. For TEM, samples were prepared by placing a drop of the catalyst suspension with ethanol on a carbon-coated copper grid. The elemental composition of the catalysts was investigated by energy dispersive X-ray spectroscopy (EDX). The molar ratio of Ir to Sn in the coating was further determined using
an inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

3. Results and discussion

3.1. The equilibrium cell volume and the lattice parameters

Fig. 1 shows the calculated $E$–$V$ functions for (Ir$_{1-x}$Sn$_x$)O$_2$, and the fitting curves based on Eq. (4). In Table 1, the calculated structure parameters of the pure IrO$_2$ and SnO$_2$ are compared with the values reported in literature and those archived by Joint Committee on Powder Diffraction Standards (JCPDS). In Fig. 2a, when lattice parameters ($a$ and $c$) are plotted against the molar fraction ($x$) of Sn in the lattice, deviation of $c$ from the Vegard’s law (linear relation) is distinct, indicating a strong interaction between the unlike cations present in the ternary system. Fig. 2b shows the calculated $V_0$ of (Ir$_{1-x}$Sn$_x$)O$_2$ as a function of $x$. $V_0$ deviates distinctly from what is calculated using the Vegard’s law. A third-order polynomial equation can be used to fit the $V_{0-x}$ relation at 0 K:

$$V_0 = 62.42 + 10.20x + 0.287x^2 - 1.207x^3 \quad (8)$$

3.2. The interaction parameter and Gibbs free energy

Besides $V_0$, fitting the $E$–$V$ curve with Eq. (4) also gives the total energies of (Ir$_{1-x}$Sn$_x$)O$_2$ ranged from $x=0$ to 1. The calculated $E_0$($0 \text{ K}$–$x$) data points in Fig. 3 are fitted with the following polynomial (in the unit of eV atom$^{-1}$):

![Image](https://example.com/image.png)

Fig. 1. The calculated dependence of the total energy on the volume of (Ir$_{1-x}$Sn$_x$)O$_2$ supercells.

![Image](https://example.com/image.png)

Fig. 2. The calculated lattice constants ($a$ and $c$ in a) and cell volume ($V_0$ in b) as a function of the molar fraction ($x$) of SnO$_2$ in the rutile solid solution phase.

Table 1
Comparison of the calculation results with the experimentally determined unit-cell lattice constants (a and c) and cell volume ($V_0$) of (Ir$_{1-x}$Sn$_x$)O$_2$.

<table>
<thead>
<tr>
<th>$x$</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>$\alpha$, $\beta$, $\gamma$ (°)</th>
<th>$V_0$ (Å$^3$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.4548</td>
<td>4.4548</td>
<td>3.1482</td>
<td>90.00, 90.00, 90.00</td>
<td>62.477</td>
<td>Present study</td>
</tr>
<tr>
<td></td>
<td>(4.452)</td>
<td>(4.452)</td>
<td>(3.120)</td>
<td></td>
<td>(63.24)</td>
<td>Present study</td>
</tr>
<tr>
<td>0.125</td>
<td>4.492</td>
<td>4.492</td>
<td>3.108</td>
<td>90.00, 90.00, 89.96</td>
<td>62.71</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>(4.472)</td>
<td>(4.472)</td>
<td>(3.159)</td>
<td></td>
<td>(61.77)$^b$</td>
<td>6</td>
</tr>
<tr>
<td>0.25</td>
<td>4.5311</td>
<td>4.5222</td>
<td>3.1737</td>
<td>90.00, 90.00, 90.02</td>
<td>65.606</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(4.5561)</td>
<td>4.5692</td>
<td>3.1862</td>
<td></td>
<td>66.328</td>
<td></td>
</tr>
<tr>
<td>0.375</td>
<td>4.6037</td>
<td>4.6037</td>
<td>3.1873</td>
<td>90.00, 90.00, 90.06</td>
<td>67.552</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(4.6628)</td>
<td>4.6522</td>
<td>3.1802</td>
<td></td>
<td>68.986</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>4.7129</td>
<td>4.7125</td>
<td>3.1851</td>
<td>90.00, 90.00, 90.00</td>
<td>70.740</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(4.7407)</td>
<td>4.7407</td>
<td>3.1919</td>
<td></td>
<td>71.736</td>
<td>Present study</td>
</tr>
<tr>
<td>1</td>
<td>(4.740)</td>
<td>(4.740)</td>
<td>(3.188)</td>
<td>90.00, 90.00, 90.00</td>
<td>(71.64)</td>
<td>Present study</td>
</tr>
<tr>
<td></td>
<td>4.834</td>
<td>4.834</td>
<td>3.244</td>
<td></td>
<td>(71.30)</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>(4.715)</td>
<td>4.715</td>
<td>3.194</td>
<td></td>
<td>74.57</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>(4.738)</td>
<td>(4.738)</td>
<td>(3.188)</td>
<td></td>
<td>(73.57)</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>(4.738)</td>
<td>(4.738)</td>
<td>(3.187)</td>
<td></td>
<td>(71.552)</td>
<td>33</td>
</tr>
</tbody>
</table>

$a$ x value in the general formula of solid-solution (Ir$_{1-x}$Sn$_x$)O$_2$.

$^b$ The values in the brackets are from experimental characterizations.

$c$ JCPDS index number.

$$E_0,(\text{Ir}_{1-x},\text{Sn}_x)\text{O}_2 = -8.39 + 1.45x + 0.277x^2 - 0.827x^3 + 0.401x^4$$

(9)

The fitting curve of total energy shows a slight positive deviation in the whole range of $x$ from the simple rule of mixing (dotted line) for an ideal solution. No doubt the positive $H^m$ provides the driving force for the reported phase separation/ segregation of a solid solution phase of the Ir–Sn–O system. Comparing Eqs. (7) and (9), $H^m$ can be obtained as Eq. (10) in the unit of kJ (mole of atoms)$^{-1}$.

$$H^m = x(1-x)(29.6 - 2.79x + 8.85x^2)$$

(10)

Thus, the interaction parameter is obtained.

$$\Omega = 29.6 - 2.79x + 8.85x^2$$

(11)

Note that Eq. (11) applies for $T = 0$ K only. Here we account for the dependence of $\Omega$ on temperature. At 0 K, $\Omega_{\text{IrO}_2}$ and $\Omega_{\text{SnO}_2}$ of 29.6 and 35.7 kJ mol$^{-1}$ atom$^{-1}$, respectively, are obtained from Eq. (11). At the temperatures close to the melting point or the decomposition temperature of a hard material, $\Omega$ has been estimated to be 10–25 kJ mol$^{-1}$ atom$^{-1}$, 24.25.35.36 Similar to the prior reports in literature, we find a negligibly small effect of the choice between 15 and 30 kJ mol$^{-1}$ atom$^{-1}$ on the final results of the temperature dependency mainly because of the large temperature range considered. In the present study, we select $\Omega = 15$ for SnO$_2$ ($B_0 = 213$ GPa) at its melting point (1923 K). $\Omega = 20$ is selected for IrO$_2$ ($B_0 = 270$ GPa)$^{32}$ at its decomposition temperature (1293 K).$^{32}$ As a result, Eqs. (12) and (13) are obtained for the exponential ($\Omega = H_0 e^{-T/T_c}$) dependency.

$$\Omega_{\text{IrO}_2}^T = 29.55 \times \exp \left(-\frac{T}{3312}\right)$$

(12)

$$\Omega_{\text{SnO}_2}^T = 35.61 \times \exp \left(-\frac{T}{2224}\right)$$

(13)

The exponential temperature dependencies of (Ir$_{1-x}$Sn$_x$)O$_2$ is estimated using the simple rule of mixing:

$$\Omega_{(\text{Ir}_{1-x},\text{Sn}_x)\text{O}_2}^T = \frac{(1-x)\times \exp \left(-\frac{T}{3312}\right) + x \times \exp \left(-\frac{T}{2224}\right)}{x}$$

(14)

![Fig. 3. The calculated total energies (open circles) by the ab initio DFT, and the fitting results (solid line) using Eq. (9) in the unit of eV atom$^{-1}$ for rutile solid-solution (Ir$_{1-x}$Sn$_x$)O$_2$. The dotted line is based on the simple rule of mix (linear $E_0$–x relation).](attachment:image.png)
To examine the temperature effect of \( \Omega \) on \( G^m \), we plot \( G^{m-x} \) relations in Fig. 4 using the temperature independency (Fig. 4a) and exponential (Fig. 4b) temperature dependency of \( \Omega \). The temperature effect of \( \Omega \) is distinct. Note that a solid solution phase possesses a higher Gibbs free energy than the corresponding simple mixture with a same overall chemical composition at a same temperature. Therefore, at the regular preparation temperatures (<650 °C) of Ir–Sn–O, the solid solution phase, even if instantaneously existing, would spontaneously decompose into IrO\(_2\) and SnO\(_2\) to lower the overall Gibbs free energy of the system (Fig. 5).

3.3. Phase diagram

To understand the stability of the solid solution phase and the nature of the phase decomposition, we calculate the derivatives of the Gibbs free energy of mixing of \((\text{Ir}_{1-x}\text{Sn}_x)\text{O}_2\) as functions of \( x \). Recall that the curve of \( \delta(G^m)/\delta x = 0 \) (binodal) dictates the boundary between the thermodynamically stable and unstable regimes, as well as the compositions of the phases in equilibrium at a specified temperature. The curve of \( \delta^2G^m/\delta x^2 = 0 \) (spinodal) dictates the virtual boundary between the spinodal immiscible regime (\( \delta^2G^m/\delta x^2 < 0 \)) and the metastable regime (\( \delta^2G^m/\delta x^2 > 0 \)). The point of \( \delta^3G^m/\delta x^3 = 0 \) dictates the temperature above which complete miscibility between the compositional phases is possible, resulting in a single homogeneous phase. Fig. 5 shows the phase stability diagrams of the IrO\(_2\)–SnO\(_2\) quasi-binary system, calculated with the temperature independent (Fig. 5a) and the exponentially temperature-dependent (Fig. 5b) \( \Omega \). As predicted, the assumption of the temperature independency of \( \Omega \) leads to an unreasonably high critical point at 5118 K in Fig. 5a. In comparison, a much lower critical point (2257 K) is obtained in Fig. 5b using the exponential temperature dependency. Fig. 5b reveals

![Fig. 5. Temperature–composition diagrams showing the spinodal (dotted curves) and binodal (dashed curves), calculated with temperature independent (a) and exponentially temperature-dependent (b) interaction parameter.](image-url)

![Fig. 4. Gibbs free energy of mixing \((G^m)\) as a function of molar fraction of SnO\(_2\) at varied temperatures, calculated with temperature independency (a) and the exponential (b) temperature dependency of the interaction parameter.](image-url)

![Fig. 6. Calculated equilibrium phase diagram of Ir–Sn–O.](image-url)
that an Ir-rich phase ("ISS" from here after) and a Sn-rich phase (SSS) coexist preferentially at temperatures above 960 K, while pure IrO2 and SnO2 phases predominate below 960 K. In the regime below the dotted curve in Fig. 5b, where $\delta^2 G^m/\delta x^2 < 0$, spinodal decomposition of (Ir1-xSnx)O2 occurs. In comparison, in the regime between the dotted and the dashed curves, where $\delta^2 G^m/\delta x^2 < 0$ but $\delta^2 G^m/\delta x^2 > 0$, the solid solution phase is thermodynamically metastable, and its decomposition follows the nucleation-and-growth mechanism. Note that the unstable regime (the regime below the dashed curve) is broad, indicating relatively low concentration of SnO2 in ISS, and IrO2 in SSS. For example, the binodal curve gives a 1.4 mol% solubility of IrO2 in SSS at 1298 K. This is in good agreement with the experimental result by McDaniel and Schneider which that 2.3 mol% solubility of IrO2 in SSS was obtained at 1298 K. Knowing the peritectic reaction temperature of 1302 K for Ir–Sn–O, and that IrO2 and SnO2 decompose at 1293 and 2773 K, respectively, we can plot the phase diagram for Ir–Sn–O in Fig. 6.

3.4. Experimental evidence for the phase separation in the spinodal region

XRD patterns of ISO320 and ISO450 are shown in Fig. 7. Rutile {1 1 0} and {1 0 1} diffraction peaks are observed for both samples. The insets in Fig. 7 show that ISO320 contains only one rutile phase (TSS), which separates into two distinctive phases in ISO450 of which the {1 1 0} peaks reside on the two sides of the initial peak observed for ISO320. This suggests a phase separation of the oxide.

In order to perform a reliable quantitative phase analysis, a $V_0$–x relation has to be established. In literature, the Vegard's law (linear relationships between lattice parameters and x) was assumed from time to time. However, as discussed in sections 3.1 and 3.2, Vegard's law does not apply correctly to Ir1-xSnxO2. On the other hand, although Eq. (8) from DFT reflects the deviation from Vegard's law because of the Ir–Sn mixing enthalpy, DFT results cannot match exactly measured $V_0$’s of IrO2 and SnO2. Thus, we introduce a correction to Eq. (8):

$$V'_0(x) = V'_0(0) + \left[ V'_0(1) - V'_0(0) \right] x$$

$$V'_0(0) + \left[ V'_0(1) - V'_0(0) \right] x$$

(15)

where $V'_0(0) = 63.24$ Å$^3$ and $V'_0(1) = 71.64$ Å$^3$ are the measured unit cell volumes of IrO2 and SnO2 listed in Table 2. As such, Eq. (15) not only reflects the intrinsic nonlinearity of $V_0$–x for Ir–Sn–O but also covers the experimental end points. The $V_0$–x relationships based on Eqs. (8) and (15), Vegard’s law are plotted and compared in Fig. 8. The phase analysis results are summarized in Table 2. Based on the lattice parameters of SSS and ISS measured by XRD, we calculated $V_0$ values for SSS and

<table>
<thead>
<tr>
<th>Oxides</th>
<th>ISO320</th>
<th>ISO450</th>
<th>IrO2</th>
<th>SnO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSS</td>
<td>$a$ (Å)</td>
<td>4.647</td>
<td>-</td>
<td>4.739</td>
</tr>
<tr>
<td></td>
<td>$c$ (Å)</td>
<td>3.170</td>
<td>-</td>
<td>3.190</td>
</tr>
<tr>
<td></td>
<td>$V_0$ (Å$^3$)</td>
<td>68.45</td>
<td>-</td>
<td>71.64</td>
</tr>
<tr>
<td></td>
<td>$x_i$</td>
<td>0.572</td>
<td>-</td>
<td>0.466</td>
</tr>
<tr>
<td></td>
<td>$f_i$</td>
<td>0.522</td>
<td>-</td>
<td>1.0</td>
</tr>
<tr>
<td>ISS</td>
<td>$a$ (Å)</td>
<td>4.624</td>
<td>4.587</td>
<td>4.502</td>
</tr>
<tr>
<td></td>
<td>$c$ (Å)</td>
<td>3.160</td>
<td>3.190</td>
<td>3.120</td>
</tr>
<tr>
<td></td>
<td>$V_0$ (Å$^3$)</td>
<td>67.56</td>
<td>66.42</td>
<td>63.24</td>
</tr>
<tr>
<td></td>
<td>$x_i$</td>
<td>0.466</td>
<td>0.342</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$f_i$</td>
<td>0.514</td>
<td>0.392</td>
<td>0</td>
</tr>
</tbody>
</table>

$^a$ Calculated composition of phase based on $V'_0$ using Eq. (15).
$^b$ Calculated composition of phase based on $V_0$ using Vegard’s law.
$^c$ Overall composition determined by ICP–AES.
$^d$ Calculated overall composition based on $V_0$ using Vegard’s law.
$^e$ Calculated overall composition based on $V'_0$ using Eq. (15).
$^f$ Relative deviation from the actual composition ($x_i$).
ISS, and then their corresponding compositions \((x_t)\) using Eq. (15). The molar fractions \((f_j)\) of SSS and ISS were then calculated following a conventional XRD quantitative phase analysis procedure. To verify the validity of Eq. (15) and the phase analysis results, we compare the calculated overall compositions \((x_t = \sum x_t f_j)\) with the measured actual compositions of ISO320 \((x_0 = 0.468)\) and ISO450 \((0.458)\). \(x_t\) agrees very well with \(x_0\). By contrast, the simple calculation \((x_s)\) based on the Vegard’s law shows \(>10\%\) deviation from \(x_0\). Therefore, the DFT-assisted XRD quantitative phase analysis is much more reliable than the conventional uncorrected phase analysis, and can be applicable for various multi-component compounds/mixtures.

The phase analysis shows that the \(\text{SnO}_2\) molar fractions of SSS \((x_t = 0.572)\) and ISS \((0.342)\) for ISO450 are larger and smaller, respectively, than that of TSS \((0.466)\) for ISO320. This agrees with the general trend in the composition change in phases as spinodal decomposition takes place. Indeed, in Fig. 6, the starting composition \((x_0 = 0.468)\) falls within the calculated spinodal regime between 5.2\% and 96\% at \(450\,^\circ\text{C}\), which means that the atomic mixture, \((\text{Ir}_{0.534}\text{Sn}_{0.466})\text{O}_2\) is unstable and would spontaneously decompose into the ISS and SSS phases. Consistent with the XRD results, HRTEM (Fig. 9a inset) shows that ISO320 is characteristic with only one rutile phase. For ISO450, two sets of rutile \((110)\) and \((200)\) spots are observed in the electron diffraction patterns (Fig. 9b inset); the one with a relatively large inter-plane space is assigned to SSS, and the other to ISS. Therefore, the HRTEM characterizations corroborate the XRD results that ISO450 is composed of ISS and SSS as the products of spinodal decomposition.

In the end, we should note that all the \textit{ab initio} calculated structures in the present study (as well as those in Refs. 23–25) are constructed at the temperature of 0 K, which is much lower than the actual synthesis temperature (typically \(>300\,^\circ\text{C}\)) of the oxide coating. From the view of theoretical calculations, there are various approaches to improving \textit{ab initio} calculation accuracy to better match experimental results at \(>0\,\text{K}\). Fortunately, the compositions of ISO320 and ISO450 from the phase analysis in Table 2 match the ICP-AES results very well \(<1\%\), suggesting that the \textit{ab initio} calculated Ir–Sn–O structures can be applied readily to room temperature and beyond. This is not difficult to understand in view of the fact that volumetric thermal expansion coefficients of most transition metal oxides are within tens of parts per million (ppm), which are negligible compared with the experimental errors from XRD and sample preparations. The \textit{ab initio} calculation-assisted quantitative phase analysis has also been proved valid for other oxide systems such as Ru–Zr–O and Ru–Sn–O.25 Regarding the thermodynamics calculations, we considered \(\Omega\) the only parameter that depends explicitly on temperature. This simplification, though widely used in literature, could cause certain deviations of the calculated phase diagram from its actual case. Besides, when studying the phase separation of a specific Ir–Sn–O catalyst with ultra-fine domains or ultra-small thickness, surface energy plays an important role in the thermodynamics calculations. These aspects are beyond the scope of the present study, but do not affect our conclusion on the spinodal nature of the phase separation for Ir–Sn–O.

4. Conclusions

The present study combines \textit{ab initio} DFT and thermodynamics calculations to calculate the Gibbs free energy of mixing for the formation of rutile phase solid solution between rutile IrO\(_2\) and \(\text{SnO}_2\). Phase diagram of Ir–Sn–O is constructed by taking into account the temperature dependency of the enthalpy of mixing. It is shown that the conventional experimental conditions and compositions fall in the broad spinodal regime; therefore, thermodynamically, complete miscibility between IrO\(_2\) and \(\text{SnO}_2\) to form a true solid solution phase is unlikely at regular sample preparation conditions. It is important to note that although the Ir–Sn–O system conforms to all the Hume–Rothery rules for the formation of a substitutional solid solution, phase separation is actually thermodynamically preferred because of enthalpy of mixing. Using XRD phase analyses and HRTEM characterizations of \((\text{Ir}_{0.534}\text{Sn}_{0.466})\text{O}_2\) coating prepared at 320 and 450 K, we confirm the spinodal phase separation of the oxides. The present fundamental study provides an important thermodynamic explanation for the phase separation of the Ir–Sn–O electrocatalyst, which could be important for microstructure engineering of the catalyst towards high catalytic activities. The DFT-assisted quantitative phase analysis is more reliable than the conventional approximations based on the Vegard’s law,
and provides an important general approach to reliable phase analysis for complex compounds.

Acknowledgements

The authors acknowledge the financial support from Natural Science Foundation of China (11104031 and 50472002), National High Technology Research and Development Projects (863) of China (2007AA03Z325), the central financial aid for innovation team building (2012-FD-02), Key International Cooperation Projects of Fujian Province (2007I002), and Natural Science Foundation of Fujian Province (2009J01239, 2009J05116 and 2013J01175).

References
