University of Leeds

Computational study of FeNbO₄based fuel electrode for Solid Oxygen Cells

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Intellectual Property and Publication Statements

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The chapter 3 and chapter 5 are based on the publications 'Wang, X.; Santos-Carballal, D.; de Leeuw, N. H., Density Functional Theory Study of Monoclinic Fenbo4: Bulk Properties and Water Dissociation at the (010), (011), (110), and (111) Surfaces. *The Journal of Physical Chemistry C* **2021**, *125*, 27566-27577', and Wang, X.; De Leeuw, N. H.; Santos-Carballal, D., Oxygen Diffusion in the Orthorhombic FeNbO4 Material: A Computational Study. *Physical Chemistry Chemical Physics* **20**23, **25**, 6797-6807', respectively. In those two papers, the candidate contributes to the theoretical investigation and the original writing. Professor Nora de Leeuw and Dr David Santos-Carballal contribute to the method development and the reviewing of manuscripts.

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Abstract

This thesis presents the results of a computational study of the bulk and surface of FeNbO₄ used as fuel electrode of solid oxygen cells (SOCs). Using density functional theory with D2 long-range dispersion correction and on-site Coulomb interactions (DFT+U-D2), we have investigated a number of properties of this material.

First, the antiferromagnetic structure of the monoclinic FeNbO₄ (m-FeNbO₄) observed experimentally is examined to be the most stable one. The dissociation of water at the pristine surfaces without introduced defects are simulated to reveal its mechanism as the cathode of solid oxygen electrolysis cells (SOECs). Secondly, the dissociation of hydrogen and the formation of water on the surfaces of orthorhombic FeNbO₄ (o-FeNbO₄) is investigated. For the surface reactions, the hydrogen prefers to dissociate in the oxygen-oxygen sites whereas the migration of the hydrogen from the metaloxygen sites are more energetically favourable. Thirdly, we have analysed the probabilities of inequivalent configurations of the o-FeNbO₄ to explain why the cations are distributed disorderedly. The oxygen diffusion in the stoichiometric and nonstoichiometric structures is investigated and it shows that the diffusion in the oxygendeficient structure is much easier than in the perfect structure and the energy barriers are affected by the surrounding oxygen type. Finally, the effect of the first-row transition metal dopants on the stoichiometric and non-stoichiometric structures are investigated. The simulations show that substituting Fe cations with dopants in the stoichiometric structure is more energetically favourable than Nb cations which leads to significant volume expansion, while the introduction of oxygen vacancies can lower the doping energies for the Nb sites. The electron conduction is strengthened especially for the Ti and V dopants into the Fe sites in all structures.

In this way, the findings presented in this thesis provide a theoretical insight into the bulk and surface properties of the FeNbO₄ materials.

Table of Contents

Intellectual Property and Publication Statements	2
Acknowledgement	3
Abstract	4
Table of Contents	6
List of Figures and Tables	11
List of Abbreviations	22
Chapter 1: Introduction	25
1.1 FeNbO ₄	25
1.1.1 Monoclinic FeNbO ₄	26
1.1.2 Orthorhombic FeNbO ₄	27
1.1.3 Synthesis method	29
1.1.4 Applications	
1.2 Solid oxygen cells	
1.2.1 Working mechanism	
1.2.2 SOCs fuel electrode	
1.3 Overview of thesis	41

Chapter 2: Computational methods	42
2.1 Schrödinger equation	42
2.2 Density Functional Theory (DFT)	43
2.2.1 The Hohenberg-Kohn Theorems	44
2.2.2 Kohn-Sham equations	45
2.2.3 Exchange correlation functional: LDA and GGA	46
2.3 DFT+ U method	47
2.4 The electronic structure problem in periodic solids	49
2.4.1 Bloch's theorem	49
2.4.2 Plane-wave expansion of the wavefunctions	50
2.5 Pseudopotentials	51
2.5.1 The projector augmented-wave (PAW) method	51
2.6 Dispersion correction method	52
2.7 Geometry optimization	53
2.8 Other computational details	54
2.8.1 Bader analysis of the charges	54
2.8.2 Density of states	55
2.8.3 Wulff shape construction and scanning tunnelling micro	oscopy (STM)
images	56
2.8.4 Transition state	56
2.8.5 Vibrational frequencies	57
2.8.6 Force field parameters	

Chapter 3: Monoclinic FeNbO ₄	60
3.1 Abstract	60
3.2 Introduction	61
3.3 Computational method	62
3.4 Bulk properties	65
3.5 Surfaces	74
3.6 Adsorption and dissociation of water	82
3.6.1 Fe site	82
3.6.2 Nb site	85
3.7 Chapter conclusion	
Chapter 4: Dissociation of hydrogen on the surfaces of o-FeNbO ₄	91
4.1 Abstract	91
4.2 Introduction	92
4.3 Computational method	94
4.4 Surface properties	97
4.5 Dissociation of H ₂	
4.5.1 (010) surface	105
4.5.2 (111) surface	
4.6 Formation of water	
4.7 Chapter conclusion	115
Chapter 5: Oxygen diffusion in the bulk	
5.1 Abstract	

5.2 Introduction		
5.3 Computation	al method	
5.3.1 Force 1	field parameters	
5.3.2 SOD n	nethod	
5.3.3 DFT si	mulations	
5.4 GULP simula	ations	
5.5 Dominant ph	ase	
5.5.1 Bulk p	roperties	
5.6 Oxygen vaca	ncies.	
5.6.1 Types	of oxygen vacancies	
5.6.2 Inequiv	valent configurations	
5.7 Oxygen Diffe	usion	
5.7.1 Stoichi	iometric structure	135
5.7.2 Non-st	oichiometric structure	
5.8 Chapter conc	lusion	
Chapter 6: Effect of I	Dopants on the o-FeNbO ₄	145
6.1 Abstract		145
6.2 Introduction		146
6.3 Computation	al method	
6.3.1 DFT ca	alculations	
6.3.2 Doping	g energy	
6.4 Stoichiometr	ic o-FeNbO4	

6.4.1 Bulk properties	151
6.4.1 PDOS	159
6.5 Non-stoichiometric o-FeNbO ₄	163
6.5.1 Bulk properties	165
6.5.2 PDOS	170
6.6 Chapter conclusion	177
Chapter 7: Conclusion and future work	179
7.1 Conclusion	179
7.2 Future work	
References	183
Appendix A	209
Appendix B	212
Appendix C	217

List of Figures and Tables

Figure 1.1. Temperature scales for the phases I, II and III of FeNbO ₄ .[3].	26
Figure 1.2. Octahedral structure of NbO ₆ (a) and FeO ₆ (b)	26
Figure 1.3. Monoclinic FeNbO4 structure.	27
Figure 1.4. Orthorhombic FeNbO ₄ structure.	28
Figure 1.5. Preparation route for the FeNbO ₄ powder.[4]	29
Figure 1.6 Schematic preparation. route for 1D nanometer fiber FeNbO ₄	.[12]
	30
Figure 1.7. Working mechanism of SOECs (left) and SOFCs (right).[35]	37

Figure 3.1. Lattice structure of FeNbO4 after optimization;	O atoms are in red;
Fe atoms are in yellow; Nb atoms are in green	66
Figure 3.2. Three different magnetic structures for	m-FeNbO4; (a):
antiferromagnetic structure 1 (AFM1); (b): antiferron	nagnetic structure 2
(AFM2); (c): ferromagnetic structure (FM); O atoms a	are in red; Fe atoms
are in yellow; Nb atoms are in green.	67

Figure 3.3. Projected of the total density states (PDOS) for the Fe, Nb and O

in the AFM1, AFM2, and FM phase70
Figure 3.4. The values of stability criteria 7-12 for AFM1, AFM2, and FM. 72
Figure 3.5. Model of the (001), (010) and (100) FeNbO ₄ surfaces and their
energies: O atoms are in red; Fe atoms are in yellow and Nb atoms are in
green.
Figure 3.6. Model of the (011), (101), (110) and (111) FeNbO4 surfaces and their
energies: O atoms are in red; Fe atoms are in yellow and Nb atoms are in
green.
Figure 3.7. Different views of the equilibrium morphology of the FeNbO4
crystal derived from a Wulff construction; a: vertical to <010> direction;
b: side view.
Figure 3.8. Calculated scanning tunnelling microscopy (STM) images of the
Figure 3.8. Calculated scanning tunnelling microscopy (STM) images of the (010), (011), (110) and (111) FeNbO ₄ surfaces: O atoms are in red; Fe
Figure 3.8. Calculated scanning tunnelling microscopy (STM) images of the (010), (011), (110) and (111) FeNbO ₄ surfaces: O atoms are in red; Fe atoms are in yellow and Nb atoms are in green
 Figure 3.8. Calculated scanning tunnelling microscopy (STM) images of the (010), (011), (110) and (111) FeNbO₄ surfaces: O atoms are in red; Fe atoms are in yellow and Nb atoms are in green
 Figure 3.8. Calculated scanning tunnelling microscopy (STM) images of the (010), (011), (110) and (111) FeNbO₄ surfaces: O atoms are in red; Fe atoms are in yellow and Nb atoms are in green
 Figure 3.8. Calculated scanning tunnelling microscopy (STM) images of the (010), (011), (110) and (111) FeNbO4 surfaces: O atoms are in red; Fe atoms are in yellow and Nb atoms are in green
 Figure 3.8. Calculated scanning tunnelling microscopy (STM) images of the (010), (011), (110) and (111) FeNbO4 surfaces: O atoms are in red; Fe atoms are in yellow and Nb atoms are in green. 81 Figure 3.9. Most stable adsorption structures of H2O on the Fe site of the FeNbO4 (011), (010), (110) and (111) at 0 K (left) and the related charge density difference (right) where isosurface value is 0.003 e/bohr³: O atoms are in red; Fe atoms are in yellow and Nb atoms are in green.
 Figure 3.8. Calculated scanning tunnelling microscopy (STM) images of the (010), (011), (110) and (111) FeNbO4 surfaces: O atoms are in red; Fe atoms are in yellow and Nb atoms are in green
 Figure 3.8. Calculated scanning tunnelling microscopy (STM) images of the (010), (011), (110) and (111) FeNbO4 surfaces: O atoms are in red; Fe atoms are in yellow and Nb atoms are in green
 Figure 3.8. Calculated scanning tunnelling microscopy (STM) images of the (010), (011), (110) and (111) FeNbO4 surfaces: O atoms are in red; Fe atoms are in yellow and Nb atoms are in green

- - Fe₃Nb₁-termination; (b) Fe₂Nb₂-termination; (c) Fe₁Nb₃-termination; (d)

Figure 4.6. Calculated scanning tunneling microscopy (STM) images of the

surfaces: (a) Fe ₃ Nb ₁ -termination; (b) Fe ₂ Nb ₂ -termination; (c) Fe ₁ Nb ₃ -
termination; (d) FesNbs-termination; O atoms are in red; Fe atoms are in
yellow; Nb atoms are in green
Figure 4.7. Fe/Nb-O dissociation sites (a-c) and O-O sites (d-f) of the (010)
surfaces; (a,d) Fe3Nb1-termination; (b,e) Fe2Nb2-termination; (c,f)
Fe ₁ Nb ₃ -termination; (d) Fe ₈ Nb ₈ -termination; O atoms are in red; Fe
atoms are in yellow; Nb atoms are in green105
Figure 4.8. Dissociation energy of H ₂ on the (010) surfaces from 0 to 900 K.
Figure 4.9. Charge transfer difference at the (a-c) Fe-O and (d-f) Nb-O sites
of the (010) surfaces after dissociation of H ₂ ; (a,d) Fe ₃ Nb ₁ -termination;
(b,e) Fe2Nb2-termination; (c,f) Fe1Nb3-termination; (d) Fe8Nb8-
termination; the isosurface value is 0.002 e/bohr ³ ; O atoms are in red; Fe
atoms are in yellow; Nb atoms are in green; H atoms are in white109
Figure 4.10. Dissociation sites of H ₂ on the (111) surface; O atoms are in red;
Fe atoms are in yellow; Nb atoms are in green110
Figure 4.11. Dissociation energy of H ₂ on the F ₈ N ₈ -terminated surface from 0
to 900 K
Figure 4.12. Charge transfer difference at the (a) Fe-O and (b) Nb-O sites of
the (111) surface after dissociation of H ₂ ; the isosurface value is 0.002
the (111) surface after dissociation of H ₂ ; the isosurface value is 0.002 e/bohr ³ ; O atoms are in red; Fe atoms are in yellow; Nb atoms are in green;

- Figure 4.13. Pathways of the water formation reaction on the (010) surface (top) and the (111) surface (bottom); O_v refers to oxygen vacancy.113
- Figure 4.14. Optimized structures after the diffusion of H atoms on the four surfaces; (a) Fe-O site of the Fe₃N_{1b}-terminated (010) surface; (b) Fe-O site of the Fe₂Nb₂-terminated surface; (c) Fe-O site of the Fe₁Nb₃-terminated surface ; (d) O_{Fe} site of the Fe₈Nb₈-terminated surface; O atoms are in red; Fe atoms are in yellow; Nb atoms are in green; H atoms are in white.

Figure 5.4. PDOS for the monoclinic FeNbO₄ (a) and the orthorhombic

FeNbO4 (b). 132
Figure 5.5. Types of oxygen vacancies in the ordered o-FeNbO4; oxygen is red,
Fe is brown, Nb is green and the red ball with black pattern represents the
oxygen vacancy
Figure 5.6. The third type of oxygen vacancy; oxygen is red, Fe is brown, Nb
is green and the red ball with black pattern represents the oxygen vacancy.
Figure 5.7. Distributions of the probabilities in the defect $2 \times 2 \times 1$ supercell (a);
the most stable No.7069 configuration (b) and the $2 \times 2 \times 2$ supercell used in
this chapter (c). 135
Figure 5.8. Stable interstitial site of the extra oxygen in the 2×2×2 supercell.
Figure 5.9. Diffusion pathway of the interstitial oxygen atom along the [001]
direction in the ordered stoichiometric structure (a), and the variation of
the total energy (b); red is oxygen, brown is Fe, green is Nb and the yellow
ball in (b) is the interstitial oxygen atom
Figure 5.10. Diffusion pathway of the interstitial oxygen atom along the [100]
direction (a) and the $[010]$ direction (b) in the NbO ₆ network of the
ordered stoichiometric structure and their related variation of the total
energy (c-d); red is oxygen, brown is Fe, and green is Nb and the yellow
ball in (c,d) is the interstitial oxygen atom137
Figure 5. 11. Diffusion pathway of the interstitial oxygen atom along the [100]

direction (a) and the [010] direction (b) in the FeO ₆ network of the ordered
stoichiometric structure and their related variation of the total energy (c-
d); red is oxygen, brown is Fe, and green is Nb and the yellow ball in (c,d)
is the interstitial oxygen atom138
Figure 5.12. Diffusion pathway of the interstitial mechanism along the [001]
direction in the ordered stoichiometric structure (a), and the variation of
the total energy (b); red is oxygen, brown is Fe, green is Nb and the yellow
ball in (b) is the interstitial oxygen atom139
Figure 5.13. Diffusion pathways of the oxygen atom along the [001] direction
(a) and the [110] direction (c) in the ordered non-stoichiometric structures
with an oxygen vacancy and their corresponding energy barriers (b and
d); red is oxygen, brown is Fe, green is Nb and the red ball with black
pattern represents the oxygen vacancy140
Figure 5.14. Diffusion pathways of the oxygen atom along the [001] direction
(a) and the [110] direction (c) in the disordered non-stoichiometric
structures with an oxygen vacancy and their corresponding energy
barriers (b and d); red is oxygen, brown is Fe, green is Nb and the red ball
with black pattern represents the oxygen vacancy142

Figure 6.2. The three magnetic structures examined in this study along with
the corresponding energies per formula; O is red, Fe is brown and Nb is
green
Figure 6.3. Optimised structures of FeNbO4 with Co, Cr, Mn, Ni, Ti and V
dopants on the (a) Fe site and (b) Nb site; O is red, Fe is brown, Nb is green
and dopants are dark blue152
Figure 6.4. Octahedral field splitting for the 3d orbitals and corresponding
electron occupation of dopants on the Fe site of FeNbO4157
Figure 6.5. Octahedral field splitting for the 3d orbitals and corresponding
electron occupation of dopants on the Nb site of FeNbO4158
Figure 6.6. Selected intrinsic ions, marked with a star, for the projected density
of states (PDOS) in the doped (a) Fe0.9375A0.0625NbO4 and (b)
FeNb0.9375B0.0625O4 structures; O is red, Fe is brown and Nb is green159
Figure 6.7. Projected density of states (PDOS) for the stoichiometric FeNbO ₄ .
Figure 6.8. Projected density of states (PDOS) of FeNbO4 doped with (a) Ti,
(b) V , (c) Cr , (d) Mn , (e) Co and (f) Ni on the Fe site162
Figure 6.9. Projected density of states (PDOS) of FeNbO4 doped with (a) Ti ,
(b) V, (c) Cr, (d) Mn, (e) Co, and (f) Ni, on the Nb site163
Figure 6.10. Optimised structures of four distinct oxygen vacancy types in the
FeNbO ₄ structure: (a) FFF; (b) FFN; (c) FNN and (d) NNN. The star
denotes the selected doning sites. O is red. Fo is brown and Nh is green

Figure 6.11. Octahedral field splitting for the 3d orbitals of Fe ²⁺ 166
Figure 6.12. The 1 st (a), 2 nd (b) and 3 rd (c) NN ions of the oxygen vacancy
selected for the PDOS in the FFF-vacancy type structures (a-c); the FFN-
vacancy type structures(d-f) and the FNN-vacancy type structures (g-i);
O is red, Fe is brown and Nb is green171
Figure 6.13. Projected density of states (PDOS) for FeNbO ₄ with different
types of oxygen vacancies (a) FFF; (b) FFN and (c) FNN173
Figure 6.14. Projected density of states (PDOS) for dopants and the 1 st nearest
neighbour (NN) Fe in the FFF-type Fe0.9375A0.0625NbO3.9375 structures
featuring (a) Ti, (b) V, (c) Cr, (d) Mn, (e) Co, and (f) Ni dopants on the Fe
site.
Figure 6.15. Projected density of states (PDOS) of the dopants, the 1 st and 3 rd
nearest neighbour (NN) Fe in the FFN-type Fe0.9375A0.0625NbO3.9375
structures with (a) Ti, (b) V, (c) Cr, (d) Mn, (e) Co, and (f) Ni dopants on
the Nb site.

after optimization
Table 3.2. Lattice parameters, magnetic moment (μ), bader charge (q) and
electronic energy (E) for AFM1, AFM2, and FM
Table 3.3. Elastic constants for AFM1, AMF2, and FM in 2×2×2 supercell.
Table 3.4. Elastic constants for monoclinic FeNbO ₄ , HoNbO ₄ [150] LaNbO ₄
[151]and YTaO4 [152]
Table 3.5. Surface energy and magnetic moment for the low-Miller index
surfaces of FeNbO4 with the FM configuration,76
Table 4.1. Average Bader charge (q) and the average magnetic moment (m_s) of
the ions on the top layers and the work function100
Table 5.1. Interatomic potential parameters used for the FeNbO4.
Table 5.2. Experimental and computational results for the monoclinic FeNbO4
lattice cell. (The experimental data of 1, and 2 show a P 2/a symmetry,
while the data of experiment 2 and 3 show a P 2/c symmetry.)126
Table 5.3. Inequivalent configurations for the orthorhombic FeNbO4127
Table 5.4. The lattice parameters and lattice energy of m-FeNbO4 and o-
FeNbO4 from GULP simulations
Table 5.5. Bader charge, magnetic moment and bond distance of the m/o-
FeNbO4 lattice

Table 3.1. Lattice parameters of FeNbO₄ and related interatomic distances

Table 5.6. Elastic constants and the mechanical properties of the m/o-FeNbO4.

Table 6.1. Lattice parameters oxides used in this chapter. 148
Table 6.2. Lattice parameters, y coordinate of dopants and volume of the
FeNbO4 structure with dopants incorporated at the Fe site152
Table 6.3. Lattice parameters, y coordinate of dopants and volume of the
FeNbO4 structure with dopants incorporated at the Nb site153
Table 6.4. Atomic Bader charges (q) in the doped FeNbO4structure. 154
Table 6.5. Atomic magnetic moments (m_s) , and valence states (VS) of the doped
FeNbO4 structure
Table 6.6. Shannon effective ionic radii (R) and doping energy (E_d) for the
doped FeNbO4 structure
Table 6.7. Lattice parameters (a, b and c), angles (α , β and γ), volume (V) and
formation energy of oxygen vacancy (E_{vac}) for the O-deficient FeNbO ₄
structure
Table 6.8. Atomic magnetic moments (m _s), valence states (VS), and doping
energy (E _d) in equations 6 and energy differences (E_t)of the O-deficient
FeNbO4 structure with dopants in the Fe site
Table 6.9. Atomic magnetic moments (ms), valence states (VS), and doping
energy (E _d) of the O-deficient FeNbO ₄ structure with dopants
incorporated into the Nb site

List of Abbreviations

SOCs: Solid oxygen cells

DFT+U+D2: Method combining a DFT Hamiltonian with a Hubbard

Hamiltonian and D2 long-range dispersion

SOECs: Solid oxygen electrolysis cells

m-FeNbO4: Monoclinic FeNbO4

o-FeNbO4: Orthorhombic FeNbO4

FNO: FeNbO₄

SOFCs: Solid oxygen fuel cells

TEC: Thermal expansion coefficient

Ni-YSZ: Ni-yttria stabilized zircona

Ni-SDC: Ni-samaria-doped ceria

Ni-GDC: Ni-gadolinium-doped ceria

IR: insulation resistance

TPB: Triple phase boundary

LCSM: La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O₃

HF: Hartree Fock

KS: Kohn-Sham

LDA: Local density approximation

GGA: Generalized gradient approximation

SIE: Self-interaction error

DFT+U: Method combining a DFT Hamiltonian with a Hubbard

Hamiltonian

NCPP: Norm-conserving pseudopotentials

USPP: Ultrasoft pseudopotentials

PAW: Projector augmented-wave

VASP: Vienna Ab-initio Simulation Package

DFT+D2: Method combining a DFT Hamiltonian with the D2 long-range

dispersion

CG: Conjugate gradients

DOS: Density of states

PDOS: Projected density of states

STM: Scanning tunnelling microscopy

LDOS: local density of states

MEP: minimum energy path

CI-NEB: climbing image nudged elastic band

NEB: nudged elastic band

GULP: General Utility Lattice Program

IP: Interatomic potential

PBE: Generalized gradient approximation density functional developed by

Perdew, Burke and Ernzerhof

VBM: valence band maximum

CBM: conduction band minimum

LBFGS: limited memory Broyden Fletcher Goldfarb Shanno

AFM1: Antiferromagnetic structure 1

AFM2: Antiferromagnetic structure 2

FM: Ferromagnetic structure

IS: Initial state

TS: Transition state

FS: Final state

LSCr: La_{0.75}Sr_{0.25}CrO₃

SQS: special quasi-random structures

ATAT: Alloy Theoretic Automated Toolkit

SOD: Site occupancy disorder

NN: nearest neighbour

FFF: oxygen vacancy coordinated by three Fe atoms

FFN: oxygen vacancy coordinated by two Fe and one Nb atoms

FNN: oxygen vacancy coordinated by one Fe and two Nb atoms

NNN: oxygen vacancy coordinated by three Nb atoms

Chapter 1: Introduction

1.1FeNbO₄

Research into FeNbO₄ has continued for nearly sixty years since its introduction as the gas sensors of hydrogen in the 1960s. So far, three main polymorphic forms of FeNbO₄ have been found under high temperatures.[1-5] Figure 1.1 shows that for temperatures below 1100 °C, FeNbO₄ exhibits the monoclinic wolframite-type structure (space group P2/c), which corresponds to FeNbO₄-III. For temperatures above 1100 °C, FeNbO₄-III is converted to FeNbO₄-II characterized by the α -PbO₂-type structure, with orthorhombic symmetry (space group Pbcn). When the temperature increases beyond 1380 °C, FeNbO₄-II gradually transforms into the third structure, FeNbO₄-I, which has the rutile-type structure with tetragonal symmetry (space group P42/mnm). For temperatures above 1450 °C, FeNbO₄-II and FeNbO₄-III phases, which dominate the research field of this material, are the focus of discussion in the next sub-sections.[3, 5]



Figure 1.1. Temperature scales for the phases I, II and III of FeNbO₄.[3]

1.1.1 Monoclinic FeNbO₄

In this structure, both Fe^{3+} and Nb^{5+} have a coordination number of six with oxygen ions, forming stable octahedra, as shown in Figure 1.2.



Figure 1.2. Octahedral structure of NbO₆ (a) and FeO₆ (b).

The Fe³⁺ and Nb⁵⁺ cations are distributed in alternate layers of the hexagonal closepacked (hcp) oxide, as shown in Figure 1.3. The reported lattice parameters a=4.649Å, b=5.63Å, c=5.006Å and $\beta=90.4^{\circ}$ show a typical monoclinic structure.[6] Researchers have combined experimental and computational methods to demonstrate that the Néel temperature of the m-FeNbO₄ is 46 K and that the ferromagnetic structure is the most stable under working temperatures.[7] The mixed valence nature (Fe^{2+}/Fe^{3+}) of the Fe ions in the Fe-O-Fe framework provides for electron conduction and the material exhibits high electrical conductivity.[8]



Figure 1.3. Monoclinic FeNbO₄ structure.

1.1.2 Orthorhombic FeNbO₄

Similar to the m-FeNbO₄, both octahedral Fe³⁺ and Nb⁵⁺ have a six-oxygen coordination in the o-FeNbO₄structure. However, the Fe³⁺ and Nb⁵⁺ cations are randomly distributed in the octahedral holes formed by the hcp oxide ions in the α -PbO₂ type structure. It has been reported experimentally, that o-FeNbO₄ has lattice parameters *a*=4.650Å, *b*=5.618Å and *c*=5.006Å, which are close to the monoclinic phase whereas the beta angle turns into 90°.[9] The Néel temperature of FeNbO₄-II appears near 30 K, leading to a ferromagnetic structure at room and high temperatures.



Figure 1.4. Orthorhombic FeNbO₄ structure.

The m- and o-FeNbO₄ structures differ in the distribution of the cations, moving from an ordered to a disordered arrangement as the temperature rises. The previous reports show that the structure with the ordered distribution of cations activated by annealing, where different domain structures are formed depending on the annealing temperature.[3, 5] In this process, well below the transition temperature the orthorhombic structure is found with a random distribution of Fe and Nb on one site, whereas the cation order and the averaged size of the cation-ordered domains will increase as the annealing temperature increases, due to the higher Fe and Nb mobility. For annealing temperatures close to the monoclinic \rightarrow orthorhombic transition temperature, it is observed that the lattice stress gradually relaxes, which is accompanied by the expansion of the antiphase boundary as the temperature rises. The material is annealed at temperatures in the stability region of the o-FeNbO₄ structure, resulting in low stress and a reduced degree of cation order. Finally, complete cation order within the domains is obtained when the temperature reaches 1000°C. Based on this process, multiple methods to synthesise FeNbO₄ have been developed, which are discussed in the next section.

1.1.3 Synthesis method

The most common preparation method for FeNbO₄ is through a solid-state reaction where iron oxide Fe₂O₃ and niobium oxide Nb₂O₅ react as follows:

$$Fe_2O_3 + Nb_2O_5 \rightarrow 2FeNbO_4$$

Its specific process is shown in Figure 1.5.



Figure 1.5. Preparation route for the FeNbO₄ powder.[4]

In this process, different types of FeNbO₄ can be obtained by controlling the calcination temperature and its later annealing rate. For instance, scientists have prepared samples with an α -PbO₂-type structure through reheating sintered samples at 1220°C for 30

minutes and taking them out to air during the cooling process, rather than in the conventional way, where the ramp rate for cooling is about 3 °C·min⁻¹.[10] Apart from the solid state reaction, other methods to prepare FeNbO4 samples include sol-gel synthesis, [11] where an essential quantity of citric acid solution is prepared using distilled water and Nb₂O₅·xH₂O is dissolved in this solution. Fe(NO₃)₃·9H₂O is added to the above solution and the ensuing solution is kept at 60°C for some hours to form a metal-complex. A poly-esterification step takes place next, after adding ethylene glycol at 90°C temperature followed by dehydration of the produced gel at 120°C. Finally, the powder is calcined at 550°C for 3h and at 1000°C for 16h to obtain

wolframite FeNbO₄.

In addition, it has been reported that a new method was developed to prepare onedimensional (1D) FeNbO₄ nanorods, [12] which are used as the anode in lithium ion batteries. This process is shown schematically in Figure 1.6.



Figure 1.6 Schematic preparation. route for 1D nanometer fiber FeNbO₄.[12]

In this route, NbCl₅ and FeCl₃·9H₂O were dissolved into absolute ethanol using

magnetic stirring at room temperature and the solution was dropped into poly-vinylpyrrolidone (PVP) gel, which was dissolved in absolute ethanol. Then the mixture was stirred to get a homogeneous viscous solution and it was loaded into a plastic syringe equipped with a steel needle to collect the composite nanofibers through electrospinning. After electrospinning, the composite film was removed and calcined at 950 °C in an air atmosphere.

1.1.4 Applications

1.1.4.1 Gas sensors

In the past, FeNbO₄ was studied for the detection of toxic and inflammable gases, such as Cl₂, CO, H₂, H₂S and liquefied petroleum gas (LPG).[6, 13-17] The previous work reported that the gas sensor characterization of the m-FeNbO₄ using compressed powders under H₂, H₂S and liquefied petroleum gas atmospheres. They found that the material has the largest gas reponse towards H₂ and H₂S (a maximum of about 50%) around 575-623 K, whereas increasing the temperature reduces the sensitivity.[6] Unlike H₂ and H₂S, the sensor gas response to LPG showed no noticeable response up to 550 K. However, as the temperature increased, the sensitivity increased and reached a maximum of about 80% near 625 K. As such, the sensitivity of FeNbO₄ towards those gases gradually become inactive at intermediate temperatures especially over 650 K. Further study showed that the sensitivity of the gas sensor to the test gas is closely related to the grain size, surface morphology and internal porosity of the sensor material. Compared with bulk materials, nanocrystalline sensor materials have a higher sensitivity to test gas owing to their high specific surface area.[6] Based on this phenomenon, scientists have used nanosized FeNbO₄ powders to investigate its sensitivity to H₂, LPG and NH₃ and they found that at 250 °C FeNbO₄ exhibited the largest sensitivity to H₂ (93%) and to LPG (92%), whereas at 300 °C the gas response of the sensor to NH₃ reached a maximum of about 52%.[8]

1.1.4.2 Photodetectors

The FeNbO₄ have shown good performance for use as photocatalyst.[18-23] For instance, it has been reported that the photo-electronic properties of o-FeNbO₄ showed a flat band potential between 0.1 and 0.4 V vs SCE (saturated calomel electrode) at a pH of 8.5 with an optical band gap of 2.08 eV.[23] The improvement of quantum efficiency is considered to be a result of the presence of [FeO₆] active centers while retaining the fundamental characteristics of the [NbO₆] octahedron.

Researchers have prepared o-FeNbO₄ nanoparticles with fewer surface defects, *e.g.* oxygen vacancies, than the particles prepared through the solid-state reaction method. These were used to investigate optical, photo-electrochemical, and photo-catalytic properties,[22] where it was found that the nanoparticles have a smaller optical band gap energy (1.93 eV) than the bulk powder prepared via the solid state method (2.04 eV), which indicates that nanoparticles are more sensitive to photon. Besides, FeNbO₄ nanoparticles have higher photocatalytic activity towards the degradation of RhB dye

solution under visible light (>420 nm), owing to their higher light absorption capacity and smaller particle size, as well as fewer surface defects.

1.1.4.3 Dielectric ceramic materials

Although FeNbO₄ is not a perovskite-structured material, research has shown its potential as a dielectric ceramic material.[24-29] For instance, it has been found that m-FeNbO₄ exhibits significant dielectric behaviour and three dielectric relaxations. The low temperature relaxation is caused by the hopping motion of the self-trapped electrons, the intermediate temperature relaxation is related to the electrons hopping between Fe²⁺ and Fe³⁺ ions, and the high temperature relaxation is believed to be derived from the Maxwell-Wagner relaxation caused by the grain boundary response.[25]

Scientists have prepared FeNbO₄ powders by sol-gel method and measured their dielectric properties within the frequency range of 10²-10⁶ Hz. They found that both the real and imaginary parts of the complex permittivity increased with temperature and the samples heated at 1200 °C had the highest dielectric constant and the highest losses.[26] The alternating current conductivity values indicated that the samples heated at 800, 1000, and 1200 °C were semiconductor materials, and the samples heated at 500 and 650 °C can be regarded as dielectric materials.

1.1.4.4 Anode of lithium-ion batteries

The electrochemical properties of FeNbO₄ as a type of lithium insertion anode material have also been studied previously.[12, 30-32] It has been reported that monoclinic FeNbO₄ exhibits a more stable reversible capacity than the orthorhombic phase. After coating with carbon, the reversible capacity of m-FeNbO₄ was improved and exhibited a steady capacity over 450 cycles (125.5mAh·g⁻¹ after 50 cycles), [30] owing to the coating with carbon causing FeNbO₄ to change into FeNb₂O₆, which allows facile transport of lithium-ions through its channels.

In addition, it has been found that Nano-FNO has an initial capacity of 475 mAh·g⁻¹, which is much higher than the Micro-FNO electrode (250 mAh·g⁻¹).[31] Moreover, after 100 cycles, Nano-FNO maintained a capacity of 200 mAh·g⁻¹, which is larger than that of the Micro-FNO electrode (45 mAh·g⁻¹). The Micro-FNO tended to suffer high stress and was easily cracked into smaller particles during charging and discharging, while Nano-FNO was stable in this process.

Similarly, nanofibrous FeNbO₄ was also prepared and employed as the anode in lithium ion batteries.[12] In this research, the resistance of nanofibrous FeNbO₄ electrodes (ES-FNO) synthesized through electrospinning had a lower value than in samples prepared through the solid state reaction (SS-FNO). The diffusion of Li⁺ in the ES-FNO electrode was also faster than in SS-FNO during charging and discharging, because the 1D crystal morphology of ES-FNO provided faster ionic conductivity than the bulk crystals of SS-FNO.

1.1.4.5 Electrode of solid oxygen cells

As mentioned above, m-FeNbO₄ materials can be used as the sensor materials to H₂ at temperatures below 400 °C, and this n-type semiconductor materials shows electronic conductivity of 10^{-6} S·cm⁻¹ at room temperature.[6] As a comparison, another type of structure, o-FeNbO₄, shows a higher conductivity of 0.025 S·cm⁻¹at room temperature than that of m-FeNbO4, when used as the fuel electrode of solid oxygen cells (SOCs).[10, 33, 34] In addition, several results obtained from experimental data have demonstrated that it has the potential to be used as anode materials of solid oxygen fuel cells (SOFCs). For example, the α -PbO₂-type materials Ti_{0.36}(Fe_{0.985}Nb_{1.015})_{0.84}O₄ as anodes in SOFCs show a longer lasting time than Ni-based cermets.[10] Furthermore, in air or under a hydrogen atmosphere, the electronic conductivity of FeNbO₄-based anodes could reach up to 10 S·cm⁻¹at 700 °C and the cell showed a maximum power density of 180 mW·cm², which is comparable to normal perovskite anodes. However, the studies on the FeNbO₄ anode so far can not provide us with a comprehensive understanding, and we need additional experimental and computational work to learn more about the mechanisms such as the oxygen diffusion and the oxidation of hydrogen molecule on the surfaces.

1.2 Solid oxygen cells

1.2.1 Working mechanism

Solid Oxygen cells (SOCs) is one of the most efficient and clean electrochemical energy converters and can operate in two opposite modes. One is the solid oxygen fuel cells (SOFCs) device where chemical energy is directly converted into electrical energy, and the other is solid oxygen electrolysis cells (SOECs) which use electrical energy to drive non-spontaneous chemical reactions, a reverse style with SOFCs.

A single SOC cell consists of three parts: cathode, electrolyte and anode, see Figure 1.7. In SOFCs, oxygen supplied into the cathode combine electrons to form oxide ions, which are transmitted to the anode through the electrolyte which separates the cathode and anode and only allows oxide ions or protons to traverse it, but not electrons. A fuel such as hydrogen, natural gas or other hydrocarbon is oxidized at anode and react with oxide ions to form *e.g.* water vapour. The continuously forming electrons will migrate to the cathode from the anode through the external circuit, thus producing the electric current. For SOECs, the reactions are opposite to SOFCs. For instance, under an external electrical voltage water or carbon dioxide molecules at cathode are reduced to produce hydrogen or carbon monoxide along with oxygen ions. These oxygen ions are migrated across electrolyte to anode where they release electrons and evolved into oxygen.


Figure 1.7. Working mechanism of SOECs (left) and SOFCs (right).[35]

Anode: $H_20 + 2e^- \rightarrow H_2 + 0^{2-}$ (SOECs) $H_2 + 0^{2-} \rightarrow H_20 + 2e^-$ (SOFCs) Cathode: $0^{2-} \rightarrow 1/20_2 + 2e^-$ (SOECs) $1/20_2 + 2e^- \rightarrow 0^{2-}$ (SOFCs) Total: $H_20 \rightarrow H_2 + 1/20_2$ (SOECs) $H_2 + 1/20_2 \rightarrow H_20$ (SOFCs)

1.2.2 SOCs fuel electrode

In this thesis, we are concentrated on exploring the properties of fuel electrodes (SOECs cathode or SOFCs anode) and for an efficient fuel electrode, there are following requirements.[36-45]:

- 1. An appropriate thermal expansion coefficient (TEC) that matches the value of other cell components (*i.e.* electrolyte).
- 2. Large electrical conductivity.
- 3. High capacity to avoid coke deposition.
- 4. Toughness (ability to absorb energy) properties and high strength.
- Chemical compatibility with adjoining components under a reducing atmosphere at the operating temperature.
- 6. High electrochemical and catalytic activity for the oxidation of the selected fuel gas.

- 7. High porosity (20-40%) for fuel supply and release of the reaction products.
- 8. Stable electronic and ionic conductive phases.

1.2.2.1 Ni-based anodes

Recent research activities focus on investigating the properties and mechanisms of the Ni-cermet electrodes, such as Ni-yttria stabilized zircona (Ni-YSZ), [46-52] Nisamaria-doped ceria (Ni-SDC) [53-56] and Ni-gadolinium-doped ceria (Ni-GDC) materials.[57-60] For instance, it has been found that the most-widely used cathode Ni-YSZ cermet exhibit excellent catalytic abilities to CO₂ electrolysis and CO₂/H₂O coelectrolysis at 800 °C.[46, 48] The polarization resistance of the cells using Ni-YSZ as cathode is highly dependent on the partial pressure of CO/CO₂, which especially affects the process of carbon decomposition and microstructural reconstruction of Ni and YSZ. For the application as the anode of SOFCs, researchers have demonstrated that under high operation temperature, the Ni-YSZ anodes exhibit good resistance to coarsening and growth of Ni particles, which leads to the degradation of performance of SOFCs in a long term. At temperature below 800 °C the Ni-YSZ cermet is able to remain an excellent catalytic ability toward the oxidation of pure H₂ and the average TEC of Ni-YSZ get much closed to the TEC of YSZ electrolyte. [50, 52] However, YSZ is an insulator material for electronic conduction and the addition of YSZ into Ni metal increases the insulation resistance (IR) of anode.

Recently, the research employing DFT methods has enabled us to gain a deeper

understanding of the mechanism at the atomic level. For instance, on the triple phase boundary (TPB) of the Ni-YSZ in SOFCs, the dissociation of H₂ molecules is energetically favourable at the Ni metal surfaces, then the dissociated H atoms tends to migrate through the Ni surface to the TPB region and react with the oxygen ions to form water molecule. Finally, water molecules desorb from surfaces, leaving new oxygen vacancies that would be filled later by another oxygen ions diffusing from the YSZ bulk phase. Out of those steps, the diffusion of oxygen in YSZ bulk is the rate-limiting step at low temperature, while the rate-limiting step turns into the migration of H from Ni to TPB at high temperatures.[61-64]

1.2.2.2 CeO₂

In addition to exploring and improving the properties of Ni-cermet electrodes, scientists have also put focus on developing alternative materials. Out of the plenty of available electrodes, doped CeO₂ materials have gained great development due to good catalytic activity, and electrochemical stability under both oxidation and reduction atmospheres.[65-71] For instance, when the nano-Au-CeO₂ composite was used as cathode materials of SOECs, a large area of Au-CeO₂-CO₂ TPBs can be formed at voltage of 2.9 eV, which greatly facilitates the reduction of CO₂.[71] In addition, it has been found that the SOFCs anode containing Pd@CeO₂ anode nanocomposites, where a Pd nanoparticle core is coated with a porous CeO₂ shell, exhibit good performance under CH₄ or H₂ atmosphere at 973 K.[66] It is worth nothing that under reducing

atmosphere surface Ce^{4+} is easily reduced to Ce^{3+} , leading to the formation of surface oxygen vacancies that serve as the active catalytic sites for the SOFCs mode.

The Density Functional Theory (DFT) studies have demonstrated that in a hydrogen atmosphere H_2 molecules prefer to dissociate on the pristine surfaces through the heterolytic pathway where two hydrogen atoms are bonded with one Ce and O respectively, rather than the homolytic pathway where hydrogen atoms are bound with two surface oxygen. In addition, after doped with trivalent cations, it shows a higher ionic conductivity and better catalytic activity than the pure CeO₂.[72-76] For instance, the doping of Sm into CeO₂ reduces the energy barrier of H₂ dissociation and H₂O formation and the doping of La lowers the formation energy of oxygen vacancies, which in turn facilitates the oxidation of H₂.[75]

1.2.2.3 Perovskite

Apart from the ceria-based anodes, the perovskite-type materials, such as $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$ (LSCM), SrMO₃ (M = Ti, Fe, V, Co and Mo) [77, 78] and MFeO₃ (M = Sr, La and Sm) [79-81], have also exhibited good potential of being used as the electrode materials of SOCs. In particular, the LSCM materials have gained much attention due to the relatively high electronic conductivity, and the previous studies have validated that the LCSM-based electrodes displays a competitive performance and higher durability than Ni-YSZ cermets for CO₂ electrolysis and H₂ catalysis at high temperature. Furthermore, the computational studies have summarized the formation energy of

oxygen vacancies follow the sequence of Co-O-Mn > Co-O-Co > Mn-O-Mn in bulk structures and the energy barrier for CO₂ electrolysis is no more than 0.6 eV which is a relatively low compared to Ni-based cermet electrode.[82, 83]

1.3 Overview of thesis

The aim of this thesis is to employ computational methods to investigate the mechanisms and properties used as the fuel electrode of SOCs. Chapter 3 provides details of the magnetic and electronic structures and the surface properties of the m-FeNbO₄ phase, as well as the adsorption and dissociation of water at the pristine surfaces. The dissociation of hydrogen and the formation of water at the (010) and (111) surfaces are explored in chapter 4. A number of terminations where cations are distributed randomly are modelled to simulate real configurations of o-FeNbO₄. Chapter 5 presents the results of main configurations the in the stoichiometric and non-stoichiometric phases and the diffusion of oxygen in the main configurations. Chapter 6 uses the bulk structures confirmed in chapter 5 and includes the results of the effect of the first-row transition dopants on the bulk and electronic structures.

Chapter 2: Computational methods

2.1 Schrödinger equation

For polyatomic complex chemical systems containing M nuclei and N electrons, the interaction and motion state of particles (electrons) can be described by the time-independent Schrödinger equation, written as:

$$E\Psi = \widehat{H}\Psi \quad (2-1)$$

where *E* represents the energy, Ψ is the wavefunction and \hat{H} refers to the Hamiltonian. The Hamiltonian \hat{H} is defined as:

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{NN} + \hat{V}_{eN} + \hat{V}_{ee} \quad (2-2)$$

where \hat{T}_N and \hat{T}_e are the kinetic energy operators of the electrons and nuclei, respectively; \hat{V}_{NN} , \hat{V}_{ee} and \hat{V}_{eN} are the potential energy operators of attractive nucleus-nucleus, repulsive electron-electron, and electron-nucleus interactions.

So, the Schrödinger equation can be written as:

$$E\Psi = \left(-\sum_{A=1}^{M} \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^{N} \frac{1}{2} \nabla_I^2 + \sum_{I=1}^{M} \sum_{J>1}^{M} \frac{Z_I Z_J}{R_{IJ}} + \sum_{I=1}^{N} \sum_{J>1}^{N} \frac{1}{r_{ij}} - \sum_{I=1}^{N} \sum_{I=1}^{M} \frac{Z_I}{r_{il}}\right) \Psi \quad (2-3)$$

where M_I is the ratio of the mass of nucleus I to the mass of an electron; the Laplace operator (∇) represents the second derivative with respect to the spatial coordinates of the nucleus or electron; r_{ij} , r_{iI} and R_{IJ} are the i^{th} - j^{th} electrons, i^{th} electron- I^{th} nucleus and I^{th} - j^{th} nuclei distances respectively; Z_I and Z_J are the atomic numbers of nuclei I and J.

To simplify the Schrödinger equation, Born and Oppenheimer [84] showed that nuclei can be considered fixed at their instantaneous position and that we can neglect the kinetic energy of the nuclei T_N and the repulsion interaction of nuclei V_{NN} , due to the large mass gap between nuclei and electrons, which leads to the following simplified equation:

$$\mathbf{E}\Psi = \left(-\sum_{i=1}^{N} \frac{1}{2} \nabla_{I}^{2} + \sum_{I=1}^{N} \sum_{J>1}^{N} \frac{1}{r_{ij}} - \sum_{I=1}^{N} \sum_{I=1}^{M} \frac{Z_{I}}{r_{iI}}\right)\Psi \quad (2-4)$$

The above equation can be solved exactly for one-electron systems without considering additional simplifications. For polyelectronic systems, there are two main methods to evaluate the coulomb repulsion between electrons, *i.e.* the Hartree-Fock (HF) and density functional theory (DFT) methods. The Hartree-Fock (HF) method aims to reduce the electronic interaction to a one-electron problem and considers every electron interacting with a mean-field of all the other electrons. The main shortcoming of the HF method is that the correlation between the movements of the electrons is not taken into account and therefore the total energy differs from the exact energy by the correlation energy. Although there are more elaborate post-HF methods based on the HF theory, methods based on the DFT are computationally less demanding and arguably better describe the electrons' interaction and exchange correlation than HF.

2.2 Density Functional Theory (DFT)

For solid state systems, DFT is considered the most useful tool to obtain approximate

results and solve the electronic interaction problem, according to the Hohenberg-Kohn theorems and Kohn-Sham equations.

2.2.1 The Hohenberg-Kohn Theorems

Hohenberg and Kohn proposed the theorems below to solve the many-body electron problem of the Schrödinger equation [85]

- i. The electron density $\rho(\mathbf{r})$ of the ground state of the system can be determined uniquely by the external potential field distribution $V(\mathbf{r})$, which also uniquely determines its wavefunction Ψ .
- ii. For any external potential $V(\mathbf{r})$, there is a functional of the total energy of the system, which is the variable part functional of the electron density. For a given external potential, the ground state energy of the system is the global minimum of the functional, and the electron density giving the minimum of the functional must be the electron density of the ground state, which can be written as:

$$E[\rho(r)] = \int V(r)\rho(r)dr + F[\rho(r)] \quad (2-5)$$

where $V(\mathbf{r})$ refers to the coulomb attraction between nuclei and electrons and $F[\rho(r)]$ contains the kinetic energy, inter-electronic coulomb repulsion, and exchange and correlation energies.

Furthermore, it is necessary to solve the problem of calculating the repulsion between electrons and thus to determine the ground state density of the system containing a number of interacting electrons, which requires the Kohn-Sham equations.

2.2.2 Kohn-Sham equations

Kohn and Sham proposed a theory which assumes that the functional of a system containing *n* non-interacting electrons acts in the same way as the system containing *n* interacting electrons, which simplifies the calculation of many-body systems. In this way the electron density can be expressed with one-electron Kohn-Sham (KS) orbitals Ψ_i as:[86]

$$\rho(r) = \sum_{i=1}^{n} |\Psi_i(r)|^2 \quad (2-6)$$

The energy of system of interacting electrons can be replaced by the total energy of the non-interacting electrons and the equation of $E[\rho(r)]$ can be written as :

$$E[\rho(r)] = T_{ne}[\rho(r)] + V_{eN}[\rho(r)] + V_{ee}[\rho(r)] + E_{xc}[\rho(r)] \quad (2-7)$$

where $T_{ne}[\rho(\mathbf{r})]$ is the kinetic energy of the non-interacting electrons; $V_{eN}[\rho(\mathbf{r})]$ is the nuclei-electron interaction; $V_{ee}[\rho(\mathbf{r})]$ is the inter-electronic repulsion and $E_{xc}[\rho(\mathbf{r})]$ is the exchange-correlation energy.

The KS equation is then used to find the one-electron orbitals which minimize the equation of energy:

$$\widehat{H}_{ks}\Psi_{i} = \left[-\frac{1}{2}\nabla^{2} - \sum_{A=1}^{M} \frac{Z_{A}}{|r-R_{A}|} + \frac{1}{2}\int \frac{\rho(r')}{|r-r'|}dr' + V_{XC}(r)\right]\Psi_{i} = E_{iks}\Psi_{i} \quad (2-8)$$

where the functional derivative $V_{XC}(\mathbf{r})$ is equal to $\frac{\delta E_{XC}[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})}$.

However, the form of the exchange-correlation energy term $E_{xc}[\rho(\mathbf{r})]$ is still unknown and approximations must be used, which are discussed in the next section.

2.2.3 Exchange correlation functional: LDA and GGA

There are two main approximations, namely the local density approximation (LDA) and the generalized gradient approximation (GGA), to the exchange-correlation energy term $E_{xc}[\rho(\mathbf{r})]$.

The basic idea of the local density approximation (LDA) is to use the exchange correlation energy of a uniform electron gas to approximate the $E_{xc}[\rho(\mathbf{r})]$ of the system. For a system with a uniform electron density, the LDA approximation considers that the electron gas in each grid point in the real space is locally uniform, and thus we can estimate the exchange correlation energy of the uniform electron gas with the same density at this position. So, in the LDA approximation, $E_{xc}[\rho(\mathbf{r})]$ can be calculated as:

$$E_{XC}^{LDA} = \int \rho(\mathbf{r}) \, \varepsilon_{XC}^{LDA} d\mathbf{r} \quad (2-9)$$

where ε_{XC}^{LDA} represents the exchange-correlation energy per particle of a uniform electron gas.

The LDA approximation works well in the calculation of metal systems, whereas the results for molecules and semiconductors are also acceptable, whether it is a covalent system or an ionic or metal system. However, there are known limitations, such as transition metal oxide systems with strong electronic correlation, where the results of LDA are very poor, because the predicted band gap is derived from the correlation between electrons.[87, 88]

In order to contain the density gradient and improve its rationality, another approximation has been developed, *i.e.* the generalized gradient approximation (GGA) which introduces the second derivative of the electron density into the functional, so

that the exchange correlation energy at the spatial lattice point is not only related to the electron density here, but also related to density gradient:

$$E_{XC}^{GGA} = \int \rho(\mathbf{r}) \, \varepsilon_{XC}^{LDA}[\rho(\mathbf{r}), \nabla \rho(\mathbf{r})] d\mathbf{r} \quad (2-10)$$

Results using GGA are better for most systems, especially the description of binding energies and bond lengths are more accurate, and semiconductor properties are slightly improved, especially the band gap.[89]

However, for strongly correlated systems, where electrons in d and f orbitals are highly localized, the problem known as the self-interaction error (SIE) limits the accuracy of DFT methods. Specifically, in a real system each electron interacts only with other electrons, whereas in the DFT and HF methods described above, electrons are not only treated as having Coulomb interaction with all others, but also with themselves and their own electron density, which is described as the "self-interaction".[90] In HF method, the SIE is corrected by the exchange term, which exactly cancels the spurious Coulomb self-interaction. However, this does not happen in the DFT method and thus, when using pure DFT to study systems with well localized electrons, especially transition metal oxides, there will be a systematic error. In order to correct this error, two methods have been developed, *i.e.* the DFT+U method.

2.3 DFT+U method

The DFT+U method is most commonly used to correct for the SIE in DFT. In this method, the addition of an energy penalty, the U parameter, accounts for intra-atomic Coulomb and exchange interactions, which enhances the effect of the on-site Coulomb

repulsion between electrons in the same d-bands. Thus, it can separate spin-paired electrons well and treats them as two groups, opening up band gaps that match experimental results. Among the existing DFT+U methods, in this thesis we have used the Hamiltonian in the version proposed by Dudarev *et al.*, where only a single effective parameter $U_{eff} = U - J$, in which U is the spherically averaged Hubbard parameter and J is the screened exchange energy, accounts for the Coulomb interaction, neglecting thereby any higher multi-polar terms. The total energy can be written as:[90]

$$E_{DFT+U} = E_{DFT} + \frac{U_{eff}}{2} \sum_{a} [\rho^{a} - \rho^{a} \rho^{a}] \quad (2 - 11)$$

where ρ^a is the atomic orbital occupation matrix.

It can be seen that the result of a DFT+U calculation depends on the value of the U_{eff} used. Thus, in order to obtain reliable and accurate results, this value should be tested to match experimental data and it only makes physical sense when U_{eff} and $[\rho^a - \rho^a \rho^a]$ are bigger than 0. Through adjusting the eigenvalue of the matrix (0 or 1), it can define the unoccupied (0) or occupied (1) d-levels, which are related to the ρ^a .

Although the DFT+U method can be used to correct both LDA and GGA approximations, GGA+U generally achieves more realistic results.

In this thesis, U_{eff} values used to fully describe the d-band of each transition metal ion depends on the functional used and the optimal U_{eff} values are determined by fitting calculated results to experimental data.

2.4 The electronic structure problem in periodic solids

From the above discussion, we can simplify the calculations by breaking down the polyatomic system into single electron expressions. Furthermore, in crystalline solids, where the calculations involve a large number of atoms and electrons, they can be simplified by taking into account symmetry elements. In this section, we discuss how plane-wave basis sets can be used to simplify the calculations.

2.4.1 Bloch's theorem

Bloch's theorem is employed to reduce the electronic problem in the solid state by considering the translational periodicity and symmetry of the crystal. Thus, for a solid with a high degree of symmetry, it can be simplified to consider only a few degrees of freedom. The wave functions of electrons in crystalline solids can be written as: [91]

$$\Psi_{i,k} = f_{i,k}(r)e^{ik\cdot r} \quad (2-13)$$

where r is the position; the wave vector k is the crystal momentum vector; $\Psi_{i,k}$ is the wavefunction of the i_{th} electron in a periodic potential, which is similar to the wavefunction of a free electron $e^{ik \cdot r}$; $f_{i,k}$ is a periodic function with the same periodicity as the crystal, which means that when the input argument is r or any translational vector T with the same periodicity $f_{i,k}$ will have same value.

 $f_{i,k}$ can be expanded as a Fourier series of vector G in the reciprocal lattice:

$$f_{i,k}(r) = \sum_{G} c_{i,k,G} e^{iG \cdot r}$$
 (2 – 14)

where the vectors G are defined by the expression $e^{iG \cdot r} = 1$.

From the above equations, we can see that wavefunctions with index k have the same solutions as those with index k + G. Thus, it is enough to find solutions only for the values of k-points in the first Brillouin zone, which is the primitive cell in reciprocal space.

In this thesis, two methods which can provide a suitable choice of k-points have been used, *i.e.* the tetrahedron method and the Monkhorst and Pack method.[92, 93]

2.4.2 Plane-wave expansion of the wavefunctions

Through substituting equation (2.14) into (2.13), each wavefunction can be expressed as an expansion in a basis set of planes waves:

$$\Psi_{i,k} = \sum_{G} c_{i,k+G} e^{i(k+G) \cdot r} \quad (2-15)$$

An accurate description of the electronic wave function can only be obtained from an infinite plane-wave basis set, but in practice, for high kinetic energy plane-waves the plane wave coefficients $c_{i,k+G}$ tend to zero, so the basis set is truncated to only take into account plane-waves with kinetic energy below this cut-off. As the plane wave coefficients $c_{i,k+G}$ are dependent on the wavefunction $\Psi_{i,k}$, the problem of solving the Kohn-Sham equation is simplified to find a set of $c_{i,k+G}$ that minimizes the energy. However, the wavefunction size, which is determined by the plane-wave cut-off, is still large for many-body systems and it is necessary to employ further approximations, such as pseudopotentials which are discussed in the next section.

2.5 Pseudopotentials

The pseudopotential approximation is employed to reduce the problem of the wavefunction size and the complexity of calculations. As the core electrons are assumed to have low chemical reactivity, the Coulomb potential of the core electrons and nucleus can be replaced by a potential which acts on the valence electrons. This assumption forms the basis of norm-conserving pseudo-potentials (NCPP), within which the nucleus region is replaced by a soft node-less pseudo-wave function with the same charge as the entire electron wave function in this region to avoid the rapid oscillation of core wavefunction.[94] Based on the NCCP approach, ultrasoft pseudopotentials (USPP) were developed. In USPP methodology, the core electron charge is allowed to vary and its variation is compensated by localized atom-centred augmentation charges.[95]

2.5.1 The projector augmented-wave (PAW) method

As discussed above, the core wavefuction oscillates rapidly and the wavefunctions of valence electrons near ion cores also oscillate rapidly, which makes it complex to describe wavefunctions accurately. The projector augmented-wave (PAW) method can solve this problem by converting these fast-oscillating wavefunctions into smooth wavefunctions that are more convenient to calculate. Thus, this is considered the most

robust pseudopotential approximation so far.[96]

In the PAW method, the wavefunction can be written as:

$$\Psi(r) = \widetilde{\Psi}(r) + \sum_{\Lambda} [\phi_{\Lambda}(r) + \widetilde{\phi}_{\Lambda}(r)] \langle \widetilde{p}_{\Lambda} | \widetilde{\Psi} \rangle \quad (2 - 16)$$

where Ψ and $\widetilde{\Psi}$ are the wavefunction and pseudo-wavefunction respectively; ϕ_{Λ} and $\tilde{\phi}_{\Lambda}$ are the one-electron Schrödinger equations for the isolated atom (partial waves) and auxiliary pseudo-partial waves respectively; \tilde{p}_{Λ} are projector functions. In this framework, Ψ has an atom-like behavior within the atomic (augmentation) regions, but it is identical to $\widetilde{\Psi}$ outside (interstitial regions). The basis set in the augmentation area is formed by the solution of ϕ_{Λ} , which has a nodal behavior. Expanding $ilde{\phi}_{\Lambda}$ to equal ϕ_{Λ} in the interstitial region can cancel out $ilde{\Psi}$ within the augmentation regions. Although equation (2.16) is exact for a complete expansion of ϕ_{Λ} , in practice this term is truncated to allow fast convergence, leading to some contribution of $\widetilde{\Psi}$ in the augmentation regions. In the PAW method, although core electrons are considered to be frozen in the atomic solutions, the full all-electron wavefunction is used to allow the calculation of properties which are dependent on the spin density and full charge. The use of the PAW method can make $\tilde{\Psi}$ converge faster than NCPP and USPP and we have used it in this thesis as implemented in Vienna Abinitio Simulation Package (VASP).[97]

2.6 Dispersion correction method

The pure DFT method fails to describe long-range electron correlations that lead to van der Waals forces. The most common form to correct DFT dispersion is the Grimme method known as DFT-D2,[98] which has been proved to predict a more accurate geometry and structure energy with a relatively low computational cost. The D2 method requires fewer fitted parameters and is less complexity than the D3 method. According to the D2 dispersion, the total energy E_{DFT-D} is calculated as:

$$E_{DFT-D} = E_{KS-DFT} + E_{disp} \quad (2-17)$$

where E_{KS-DFT} is conventional Kohn-Sham DFT energy and E_{disp} is an empirical dispersion correction which can be experssed as:

$$E_{disp} = -S_6 \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{C_6^{ij}}{R_{ij}^6} f_{dmp} (R_{ij}) \quad (2-18)$$

Where N is the number of atoms in the system, C_6^{ij} is the dispersion coefficient for atom pair ij, S_6 is a global scaling factor that depends on the DFT functional used, R_{ij} is an interatomic distance and f_{dmp} is a damping function used to avoid nearsingularities for small interatomic distances. f_{dmp} can be calculated as:

$$f_{dmp}(R_{ij}) = \frac{1}{1 + e^{-d(R_{ij}/R_r^{-1})}} \quad (2 - 19)$$

where d is damping parameter and R_r is the sum of the atomic van der Waals radii of the atoms i and j.

2.7 Geometry optimization

In addition to the crystal lattice parameters, the equilibrium structure also depends on the nuclei coordination in a cell unit. In the equilibrium geometry, where the difference between remaining forces are below a certain threshold, there is no net force acting on any nucleus. If the force acting on the atom in a given atomic configuration is calculated, the atom may relax towards its equilibrium position to minimize the total energy and forces. Next, it will recalculate the charge density and forces after each set of atomic movements and the process is iterated until the atomic positions have converged with respect to the forces and the gradient of potential energy surface. This whole process is known as geometry optimization.

Among several algorithms, the conjugate gradients approach (CG) is one of the most commonly used methods to locate the minimum of a function with several variables.[99] In this method, the first step is to find the minimum energy that is opposite to the direction of the maximum energy gradient, which refers the direction where the energy drops the fastest. Each direction is obtained from:

$$d_k = \Delta E_k + \gamma_k d_{k-1} \quad (2-20)$$

Where the direction d_k , which starts from point γ_k , is computed from the gradient at the point of previous direction of d_{k-1} , and γ_k can be written as:

$$\gamma_k = \frac{\Delta E_k \cdot \Delta E_k}{\Delta E_{k-1} \cdot \Delta E_{k-1}} \quad (2-21)$$

As shown above, the in this method each direction is selected from the information of all previous (conjugate) directions to find the minimum value within steps.

2.8 Other computational details

2.8.1 Bader analysis of the charges

Based on the Lewis model and the Valence Shell Electron Pair Repulsion model, Bader proposed the 'atoms in molecules' theory in which molecules are divided into atoms.[100-103] This theory is based on the electronic density and its gradient, which can be obtained from DFT calculations. Generally, the chemical bond between two atoms has the highest electron density between the two nuclei in which the electron density gradient vectors start and end. In this theory, the electron density is divided into multiple subsystems, which are separated by zero flux surfaces. The zero-flux surface is a two-dimensional surface, where the charge density is a minimum perpendicular to the surface. The volume enclosed by this surface is called the Bader Basin, in which the electron density is integrated to find the atomic charge.

2.8.2 Density of states

Unlike gas system, in a solid system with a large number of atoms, the energy levels are very close, thus forming a continuous energy band. A high density of states (DOS) means that there are many states available at this energy level, and a DOS of zero means that no available states are occupied at this energy level. Normally, there are two types of bands, the valence band, which contains the occupied state with the highest energy, and is below the Fermi level (E_F); and the conduction band, which includes the unoccupied state, and is above the Fermi level. The DOS also contains information about the site-projected DOS (PDOS), which are essential to study the bands involved in chemical bonds. There are two different spin channels, α (spin up) and β (spin down) states which are always represented by the values above and below the x axis respectively. Changes in its intensity and position indicate charge transfer and ionic or covalent interactions.

2.8.3 Wulff shape construction and scanning tunnelling microscopy (STM) images

The Wulff construction method [104] is used to determine the thermodynamic shape of a crystal and its conception can be expressed by the following equation:

$$\frac{\gamma_i}{h_i} = constant \quad (2-22)$$

where γ_i represents the surface free energy and h_i represents the distance between this surface and the polyhedron center. As the equation describes, after obtaining the free energy of different crystal faces, a thermodynamic equilibrium crystal shape can be constructed.

Employing the HIVE software, [105] we can simulate STM images of different surfaces, which is based on the Tersoff–Hamann approach where the STM tip approximates an infinitely small point source. When simulating STM images, the tunneling current between the surface and the tip is proportional to the local density of states (LDOS), integrated between the Fermi energy and the sample bias, which means that we can obtain a clear image with a suitable bias value.

2.8.4 Transition state

A transition state is the saddle point which has the highest energy on the minimum

energy path (MEP) along the reaction coordinate. In this thesis, we have used the climbing image nudged elastic band (CI-NEB) method to find saddle points between a reactant and product state. The CI-NEB method was developed from the nudged elastic band (NEB) method [106, 107] where a number of intermediate images along reaction path are inserted between reactant and product. The optimization of all images is performed simultaneously and a spring force is added between neighbouring images to maintain continuity of strap like an elastic band. In the optimization process, the forces on the atoms are continuously reduced until the minimum energy on the path is found. Compared to NEB method, the image with the highest energy in the CI-NEB method is driven up to the saddle points and not constrained by the spring force along the band. The force at this image along the tangent is reversed. Thus, this image is allowed to maximize its energy along the band and minimize its energy in all other directions and after convergence it will be at the saddle point, which can be further confirmed by the unique imaginary vibrational frequency along the reaction direction.

2.8.5 Vibrational frequencies

In any optimised geometry, the first derivative of potential energy is zero. The second derivatives have positive values, which means the vibrational frequencies are all real. However, the transition state has one imaginary frequency related to the reaction coordinate.

When calculating vibrational frequencies in VASP, each ion is allowed to move along

each Cartesian coordinate direction, and the second derivatives of a potential are calculated from the variation of energy gradient in these displacements, resulting in the Hessian matrix (a matrix of second derivatives of energy to atomic positions). This vibration frequency is determined by the eigenvalues of the Hessian matrix.

2.8.6 Force field parameters

In this thesis, the General Utility Lattice Program (GULP) code [108-111] was employed to carry out the calculations for some bulk properties including lattice parameters and elastic constants and interatomic potential (IP) fitting calculations, where the Born model for solids was implemented which describes the interaction within ions through short-range repulsive, dispersive attractive and long-range Coulombic interactions).[112] Thus, we combined the Buckingham potential with the electrostatic interactions to express the short- and long-range interactions between ions, which is given in the follows:

$$E_{ij}(r_{ij}) = A_{ij} \exp\left(\frac{-r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} + \frac{q_i q_j}{4\pi\varepsilon r_{ij}} \quad (2-23)$$

where r_{ij} is the distance between ion *i* and ion *j*, A_{ij} , ρ_{ij} , and C_{ij} are the Buckingham potential parameters for the *i*-*j* pairs and the final term $\frac{q_i q_j}{4\pi\varepsilon r_{ij}}$ is the Coulomb potential between the ion *i* and *j*. Generally, the attraction term $-\frac{C_{ij}}{r_{ij}^6}$ is always ignored when used to describe the interactions between cations and anions, since it is very small compared to the Coulombic attraction, and usually the distance between cations in oxide lattice is so far that we could also omit this short-range interaction. In

addition, we applied the shell model potential of Dick and Overhauser for the polarizable oxygen ions where the total charge of the oxygen anions is split into a massive core part and a massless shell part. The core-shell couple connected with each other through a harmonic spring could be expressed as Eq (2-24):

$$E_{cs}(r_{cs}) = \frac{1}{2}k_{cs}r_{cs}^2 \quad (2-24)$$

where k_{cs} is the spring constant and r_{cs} is the offset distance within the core-shell couple. In the core-shell model, the shell is screened Coulombically from the core and all forces including both short- and long-range interactions act on the shell, while only the long-range Coulomb force acts on the cores. Furthermore, we only applied the shell model to the anions (O²⁻), since the oxygen anions show much more polarizability than the cations (Fe³⁺ and Nb⁵⁺).

Chapter 3: Monoclinic FeNbO₄

3.1 Abstract

M- and o-FeNbO₄-based materials have been developed for many applications, including hydrogen sensors and SOECs electrodes. In this chapter, we have employed DFT calculations to investigate the bulk and surface properties of the monoclinic FeNbO₄ structure, as well as water adsorption and dissociation on its pristine surfaces. Our calculations show that the high-spin state Fe^{3+} cations have a relatively smaller Bader charge than the Nb⁵⁺ cations, which accounts for Nb–O bonds that are stronger than Fe–O bonds. The analysis of the DOS shows that the O 2p orbital occupies most of the valence band maximum (VBM), with negligible contributions from the 4d and 3d orbitals of Nb and Fe cations, respectively. We found that the 3d orbitals of Fe occupy the conduction band minimum (CBM), which explains that electrons are conducted via the Fe-O-Fe framework. The calculation of the elastic constants demonstrates that pure m- FeNbO₄ is mechanically stable. We have also considered the thermodynamic stability and structures of the seven low-Miller-index surfaces and found that the (010) facet has the lowest surface energy and expresses the largest area in the Wulff crystal shape of the particle. Finally, we have simulated the interaction of water with the Fe³⁺ and Nb⁵⁺ sites of the four most stable surfaces and found that the

dissociative adsorption of water takes place only on the (110) surface, which has important implications for the use of this material as a SOECs electrode.

3.2 Introduction

In recent years, research has intensified into the development of the ABO₄-type oxides, including iron niobate (FeNbO₄).[10, 21, 33, 113-125] As mentioned in chapter 1, three different FeNbO₄ phases have been reported, *i.e.* m-FeNbO₄, o-FeNbO₄, and r-FeNbO₄.[3] Under ambient conditions, m-FeNbO₄ has the most stable structure, where both Fe³⁺ and Nb⁵⁺ are coordinated by six oxygen ions, forming stable octahedra. In addition, the Fe³⁺ and Nb⁵⁺ cations are distributed in an ordered fashion along zig-zag chains of [FeO₆] and [NbO₆] octahedra.[1-3] The m-FeNbO₄ phase is stable up to 1050 °C, which is the temperature at which the cation distribution becomes disordered. The complete phase transformation is observed near 1100 °C with the resulting materials showing a typical α -PbO2 and rutile-type structure in the range of temperatures 1100 - 1380 °C and 1380 -1450 °C, respectively.[3, 15]

Out of the three iron niobate phases, m- and o-FeNbO₄ are promising materials for many applications. For example, m-FeNbO₄ has excellent potential as a gas sensor material, owing to its good electrical properties due to the similar radii but different valence states of the Fe and Nb cations, [6, 8, 13, 14] whereas o-FeNbO₄ has been investigated as a photodetector for solar energy conversion devices and an anode material in SOFCs.[10, 17, 19, 21] Interestingly, both m- and o-FeNbO₄ have shown

potential as a replacement material for the Ni metal in the cathodes of SOECs, [33, 34] where the splitting of water vapour takes place.

However, no computational studies have been carried out on the surface properties and reactions with gases, especially the water vapour splitting, of the m-FeNbO₄ phases. In this chapter, we have DFT methods to study the bulk and surface properties, as well as water molecule adsorption and its dissociation reaction, on the m-FeNbO₄ material.

3.3 Computational method

In this chapter, all DFT calculations were carried out using the Vienna Ab initio Simulations Package, VASP (version 5.4.4).[126-129] The projector-augmented wave method (PAW) [96] and the generalized gradient approximation (GGA)[130] with the Perdew-Burke-Ernzerhof (PBE) density functional were used to describe the ionelectron interaction and the exchange-correlation interaction, respectively. All calculations were performed using spin-polarization with Blöchl corrections. We have treated the following as valence electrons: $Fe(3p^63d^74s^1)$, $Nb(4p^65s^14d^44s^2)$, $O(2s^22p^6)$ and H(1s). To describe the electronic structures, we have used the on-site Coulombic interaction (DFT+U) [90] for the Fe 3d electrons with an U-J value of 4.3 eV.[131, 132] Following a series of test calculations, the kinetic energy cutoff for the plane wave basis was set at 500 eV. The Henkelman algorithm was used to calculate Bader charges.[133] The FeNbO4 bulk unit cell used in this chapter is the 1×1×1 P/2c monoclinic cell and the surface models were obtained using METADISE.[134] After cleaving the surfaces, we relaxed the top half of the atom layers and kept the bottom half of layers fixed at their bulk positions. All calculations of the surface and bulk are carried out with the DFT-D2 method implemented in VASP to incorporate the Van der Waals correction.[98] The surface energies of the relaxed (γ_r) and unrelaxed (γ_u) systems can be obtained through the following equations:[135-138]

$$\gamma_u = \frac{E_{slab,u} - E_{bulk}}{2A} \quad (3-1)$$
$$\gamma_r + \gamma_u = \frac{E_{slab,r} - E_{bulk}}{A} \quad (3-2)$$

where $E_{slab,u}$ and $E_{slab,r}$ refer to the total energy of the unrelaxed and half-relaxed slabs, respectively; E_{bulk} refers to the energy of the bulk containing the same number of formula units as the surface; A refers to the surface area of one side of the slab. In addition, $6 \times 6 \times 6$, $4 \times 4 \times 1$ and $1 \times 1 \times 1$ gamma-centered Monkhorst Pack grids were used for the simulation of the bulk, surface slabs and isolated water molecule, respectively. The water molecule was modelled inside a large box of $10 \times 10 \times 10$ Å³.

All calculations of the bulk and surface and the water adsorption and dissociation reaction were performed with the conjugate gradients method with a convergence criterion of 0.01 eV/Å. For the adsorption calculations, we added a single water molecule above the pristine surfaces. In addition, we employed the climbing image nudge elastic band (CI-NEB) method [139] to study the transition states between the molecular adsorption and the dissociated states of water. For the transition states, we inserted four images along the minimum energy path (MEP) to calculate the saddle points, where the calculations were carried out using the limited memory Broyden Fletcher Goldfarb Shanno (LBFGS) method [140] until the forces were smaller than

0.05 eV/Å. We confirmed that each transition state has an imaginary vibrational frequency along the reaction direction.

The variation of the Helmholtz free energy (ΔF) in the process of adsorption and dissociation can be expressed as:

$$\Delta F = \Delta H - T \Delta S \quad (3-3)$$

where ΔH is the change in enthalpy, *T* is the temperature and ΔS is the change in entropy.

For a solid phase, ΔF can be calculated as:[141]

$$\Delta F = \Delta E_{DFT} + \Delta E_{ZPE} - T\Delta S \quad (3-4)$$

where ΔE_{DFT} , ΔE_{ZPE} , and ΔS are the variation of the electronic energy obtained from the DFT calculations, the zero-point energy correction, and the vibrational contribution to the entropy, respectively. In this chapter, ΔE_{ZPE} and ΔS have been obtained by calculating the vibrational frequencies, as shown in the Appendix A. The thermodynamic data for gaseous H₂O are obtained from experimental data.[142] The ΔE_{DFT} for the adsorption and dissociation of H₂O on the surfaces can be expressed as:

$$\Delta E_{DFT} = E_{sur+adsorbate} - (E_{sur} + E_{H_20}) \qquad (3-5)$$

where $E_{sur+adsorbate}$ represents the total energy of the surface-adsorbate system, E_{sur} represents the total energy of the pristine surface and E_{H_2O} represents the energy of the isolated gas H₂O molecule.

In this chapter, the adsorption free energy was calculated at the representative temperatures of 0, 300 and 600 K under a pressure of 1 atmosphere. Once adsorbed at

the surfaces, the water molecule is treated as a part of the solid phase.

The equilibrium morphology of a FeNbO₄ particle was constructed by means of the Wulff method, where the free energy of a given surface is proportional to the distance from the center of the polyhedron to that surface. Under the conditions of our calculations, *i.e.* at 0 K and in the absence of oxygen vapor, the surface energy obtained through static calculations is equal to the surface free energy ($\sigma(T, p)$), since the surface slab has the same stoichiometry of the bulk. This method has been shown to describe successfully particle morphologies of many materials.[135, 143-145] The scanning tunnelling microscopy (STM) images of the exposed surfaces of FeNbO₄ were calculated using the Tersoff-Hamman approach as implemented in HIVE.[105] We selected a range from -1.7 eV to the Fermi level to integrate the partial charge density of the STM images.

3.4 Bulk properties

The structural parameters of FeNbO₄ after optimization are listed in Table 3.1. The computational prediction of the lattice parameters compares very well with the experimental values, as the deviation is within 1.5 %. The optimized β angle is not 90 ° (90.4 °), again in agreement with the conditions of a monoclinic structure, and has the same value as in experimental reports (90.4 °), and the bond lengths are shown in Figure 3.1.

	Fe-O (Å)	Nb-O(Å)	<i>a</i> (Å)	b (Å)	c(Å)	α(°)	β(°)	γ(°)
Simulated	2.030	2.170	4.687	5.691	5.038	90	90.4	90
(experiments)[2]	(2.014)	(2.161)	(4.637)	(5.607)	(4.992)	(90)	(90.1)	(90)
	1.997	1.981						
	(1.927)	(2.008)						
	2.109	1.901						
	(2.115)	(1.858)						

Table 3.1. Lattice parameters of FeNbO4 and related interatomic distances after optimization



Figure 3.1. Lattice structure of FeNbO₄ after optimization; O atoms are in red; Fe atoms are in yellow; Nb atoms are in green.

Furthermore, we have employed an initial high-spin electron distribution for the Fe³⁺ cations (5.2 μ_B) to study the effect of different spin configurations on the magnetization properties of the bulk. We have set up a 2×2×2 supercell, where we considered two antiferromagnetic configurations and the ferromagnetic structure, which are denoted as AFM1, AFM2, and FM, respectively. As shown in Figure 3.2, adjacent Fe³⁺ layers perpendicular to the [100] direction have antiparallel spin orientation in AFM1, whereas AFM2, in contrast, is characterised by antiparallel spin orientation within each Fe³⁺

layer.



Figure 3.2. Three different magnetic structures for m-FeNbO₄; (a): antiferromagnetic structure 1 (AFM1); (b): antiferromagnetic structure 2 (AFM2); (c): ferromagnetic structure (FM); O atoms are in red; Fe atoms are in yellow; Nb atoms are in green.

For the FM configuration all Fe³⁺ cations have the same spin orientation. The calculated bulk properties are listed in Table 3.2, which shows that the effect of the magnetic ordering on the lattice parameters, the atomic Bader charges (q) and magnetic moments (μ) are insignificant for FeNbO₄. Specifically, as expected Nb atoms lose more electrons than Fe and thus form stronger bonds with O. The Fe cations have a large calculated value of 4.27 μ B, which is close to experiment (4.66 μ B), [7] indicating that these cations are in a high spin state, in both spin channels. Unlike the Fe cations, Nb loses all of its 4d valence electrons and thus has a very low, almost zero value of μ . Remarkably, the ground state energy differences of these three types of magnetic spin configurations for m-FeNbO₄ are negligible (maximum ~0.04 eV/unit cell), that even if we were to take the AFM1 structure as the most stable structure, in agreement with earlier assumptions, [7, 146, 147] it is likely that there will be a mixture of the three magnetic structures occurring, potentially in different domains of the material.

	AFM1	AFM2	FM
<i>a</i> (Å)	4.687	4.685	4.687
b (Å)	5.684	5.683	5.684
<i>c</i> (Å)	5.033	5.034	5.033
β(°)	90.48	90.42	90.44
<i>m_{sFe}</i> (µ _B)	4.27/-4.27	4.27/-4.27	4.27
<i>m_{sNb}</i> (µ _B)	~0	~0	~0
<i>mso</i> (µB)	~0	~0	~0
q_{Fe} (e)	+1.89	+1.89	+1.89
<i>q_{Nb}</i> (e)	+2.72	+2.72	+2.72
<i>qo</i> (e)	-1.16/-1.30	-1.16/-1.30	-1.16/-1.30
<i>E</i> (eV/u.c.)	-98.133	-98.132	-98.092

Table 3.2. Lattice parameters, magnetic moment (m_s) , bader charge (q) and electronic energy (E) for AFM1, AFM2, and FM.

The PDOS plots of the three magnetic structures of m-FeNbO₄ are shown in Figure 3.3, where the distribution of bands near VBM and the CBM as well as their band gap energy (~2 eV) are very similar, which is very close to the experimental value (1.81-2.2 eV).[146] In all three phases, the O 2p orbital occupies almost the entire valence band, including its maximum (VBM) with negligible contribution from the Nb and Fe cations. Moreover, the t_{2g} and e_g orbitals of Fe (3d) occupy most of the β channel of spins of the conduction band, including the CBM, with minor contribution in the α

channel. The t_{2g} and e_g orbitals of Nb (4d) mostly occupy both the α and β channels in the conduction band far from the CBM. This result is consistent with the high and low spin state of the Fe and Nb ions, respectively. In addition, both the Fe and Nb t_{2g} orbitals occupy a larger area than the e_g orbitals in the conduction band, showing the distribution priority of electrons when there is a charge transfer process. So far, our results suggest that the electron conduction mechanism involves a promotion from the O 2p (VBM) to the Fe 3d orbitals (CBM), *i.e.* in the Fe-O-Fe framework, which corresponds to experimental results.[147] We have also demonstrated that the spin configuration have a minimal impact on the bulk properties of the material and therefore subsequent calculations were carried out using the FM phase for the sake of simplicity.



Figure 3.3. Projected of the total density states (PDOS) for the Fe, Nb and O in the AFM1, AFM2, and FM phase.

Finally, we have calculated the elastic constants C_{ij} where the finite difference technique was employed to determine the elastic tensor by performing finite distortions in the direction of each Cartesian coordinate of the lattice and deriving C_{ij} through the stressstrain method as: [148, 149]

$$C_{ij} = \frac{1}{V} \frac{\partial^2 E}{\partial \varepsilon_i \partial \varepsilon_j} \quad (3-7)$$

where *E* is the total energy of the stressed cell, *V* is the equilibrium volume and ε is the component of the applied strain. For the AFM1, AFM2, and FM spin configurations of FeNbO₄, there are 13 independent elastic constants (C₁₁, C₂₂, C₃₃, C₄₄, C₅₅, C₆₆, C₁₂, C₁₃, C₂₃, C₁₅, C₂₅, C₃₅ and C₄₆), which are listed in Table 3.3. It is clear that the elastic

constants for the three phases are virtually the same, demonstrating that the spin orientation has a negligible influence on the mechanical properties.

Table 5.5. Elastic constants for AFN11, AMF2, and FM in 2~2~2 supercen.						
Elastic constant	AFM1	AFM2	FM			
C11 (GPa)	268.9	268.8	274.1			
C ₂₂ (GPa)	273.8	271.3	269.8			
C33 (GPa)	318.8	320.4	318.8			
C44 (GPa)	75.1	73.4	74.5			
C ₅₅ (GPa)	102.5	102.9	102.1			
C66(GPa)	59.0	59.1	57.1			
C ₁₂ (GPa)	142.4	141.6	144.1			
C ₁₃ (GPa)	145.6	146.0	148.5			
C ₂₃ (GPa)	121.8	119.7	119.7			
C ₁₅ (GPa)	-6.7	-6.8	-6.8			
C25 (GPa)	-11.4	-11.5	-11.7			
C35 (GPa)	-22.4	-22.7	-22.9			
C ₄₆ (GPa)	9.7	9.7	10.2			

Table 3.3 Flastic constants for AFM1 AME2 and FM in 2X2X2 supercall

The twelve stability criteria that monoclinic phases must meet are listed in the follows.

 $C_{11} > 0, C_{22} > 0, C_{33} > 0, C_{44} > 0, C_{55} > 0, C_{66} > 0$ (Criteria 1-6);

 $[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})] > 0$ (Criteria 7);

 $(C_{33}C_{55} - C_{35}^2) > 0$ (Criteria 8);

 $(C_{44}C_{66} - C_{46}^2) > 0$ (Criteria 9);

 $(C_{22} + C_{33} - 2C_{23}) > 0$ (Criteria 10);

 $[C_{22}(C_{33}C_{55} - C_{35}^2) + 2C_{23}C_{25}C_{35} - C_{23}^2C_{55} - C_{25}^2C_{33}] > 0$ (Criteria 11);

 $\{2[C_{15}C_{25}(C_{33}C_{12} - C_{13}C_{23}) + C_{15}C_{35}(C_{22}C_{13} - C_{12}C_{33}) + C_{25}C_{35}(C_{11}C_{23} - C_{12}C_{13})] [C_{15}^{2}(C_{22}C_{33}-C_{23}^{2})+C_{25}^{2}(C_{11}C_{33}-C_{13}^{2})+C_{35}^{2}(C_{11}C_{22}-C_{12}^{2})]+C_{55}(C_{11}C_{22}C_{33}-C_{11}C_{23}^{2})$ $-C_{22}C_{13}^2 - C_{33}C_{12}^2 + 2C_{12}C_{13}C_{23} > 0$ (Criteria 12)

As to the first 6 criteria, it is clear that all of the C_{ij} (i,j=0, 1, 2, 3, 4, 5 and 6) values in Table 3.3 are greater than 0. For criteria 7-12, we have calculated their values shown in Figure 3.4, which all exceed 0 by different orders of magnitude, thereby demonstrating that the bulk material is mechanically stable.



Figure 3.4. Values of stability criteria 7-12 for AFM1, AFM2, and FM.

Here, we have selected the elastic constants calculated for the FM configuration using the $1 \times 1 \times 1$ supercell of FeNbO₄ (P 2/c) to discuss our results and compare them to other types of ABO₄ materials in Table 3.4.
Elastic constant	FeNbO ₄ (P 2/c)	HoNbO ₄ (P 2 ₁ /c)	LaNbO4 (I 2/a)	YTaO4 (I12/a1)
C ₁₁ (GPa)	274.1	387.8	242.0	354.9
C ₂₂ (GPa)	269.8	292.3	177.0	291.9
C33 (GPa)	318.8	383.4	212.0	343.0
C ₄₄ (GPa)	74.5	44.6	43.9	88.1
C55 (GPa)	102.1	30.8	11.8	82.8
C66(GPa)	57.1	51.9	53.6	73.5
C ₁₂ (GPa)	144.1	147.8	83.8	112.3
C ₁₃ (GPa)	148.5	194.9	185	146.1
C ₂₃ (GPa)	119.7	141.3	49.8	122.5
C ₁₅ (GPa)	-6.8	-35.3	4.1	1.0
C25 (GPa)	-11.7	-2.7	-16.4	-20.3
C35 (GPa)	-22.9	15.2	29.3	-57.5
C ₄₆ (GPa)	10.2	7.0	-8.9	-1.6

Table 3.4. Elastic constants for monoclinic FeNbO4, HoNbO4 [150] LaNbO4 [151] and YTaO4 [152].

Few experimental studies of monoclinic ABO₄ structures have discussed elastic constants, and in Table 3.4 we have therefore compared with computational results on other monoclinic ABO₄ materials, which shows a similar trend. As regards parameters C_{11} , C_{22} and C_{33} which measure the stiffness along the a, b and c Cartesian directions, respectively, C_{22} (269.8 GPa) is smaller than both C_{11} (274.15 GPa) and C_{33} (318.86 GPa), indicating that m-FeNbO₄ is softer along the b direction, which is the same trend as seen in the HoNbO₄ (space group P 2_1 /c) structure, where the values of C_{11} , C_{22} and C_{33} are 244.3 GPa, 231.2GPa and 272.1 Gpa, respectively.[150] As to C_{44} , C_{55} and C_{66} , which are linked to the shear deformation of the (100), (010) and (001) along the b, c and a directions, respectively, C_{66} has the lowest value (57.07 GPa), demonstrating that it is easier for the m-FeNbO₄ phase to shear in the (001) surface along the a direction than in the other two directions, which differs from the calculated results for HoNbO₄, LaNbO₄ (space group I 2/a) and YTaO4 (space group $I_{12}/a1$) where the value of C_{55} is

the lowest.[152] Finally, C_{15} , C_{25} and C_{35} are associated with the shear strain in the x-z plane when adding a stress along the a, b and c directions in the (100), (010) and (001) surfaces, respectively. Their values are negative, which shows that the β angle will decrease when a tensile stress is applied along the a, b or c direction, which could be also seen in the monoclinic HoNbO₄, LaNbO₄ and YTaO₄ structures.

In a summary, we have demonstrated that the bulk properties would not be affected in a large degree by the spin direction of Fe^{3+} and thereby in order to simplify the calculations in the following section we would take $1 \times 1 \times 1$ FM unit cell to build the surface models.

3.5 Surfaces

The m-FeNbO₄ lattice shows a high degree of asymmetry, as discussed above, and in order to identify the lowest energy and exposed surfaces for potential water adsorption and dissociation, it is necessary to consider all inequivalent low-Miller index facets. We have therefore calculated the surface energies of the different terminations of each of the 7 lowest Miller index surfaces, listed in Table 3.5. We also determined the type of surface terminations obtained, according to Tasker's method, [153] which identifies three types of surfaces (type I, II, and III), depending on the stacking of the planes of different types of atoms in an ionic crystal. In a type I surface, the overall charge of each plane is zero due to its stoichiometric ratio of cations and anions, which makes it a non-polar surface. In a type II surface, any dipole moments are cancelled out due to

the symmetrical stacking of three charged planes. However, in a type III surface, charged planes are stacked in an alternating sequence, which causes a net dipole moment perpendicular to the direction of the stacking of the planes. As a result, type I or II surfaces are stable and do not reconstruct, since there is no net dipole perpendicular to the stack direction within the stoichiometric repeat unit. A type III surface, on the other hand, needs to be reconstruction to remove the net dipole, which we have achieved by moving half of the ions from the top layer to the bottom of slab to cancel out their dipole moments, thereby obtaining a surface slab with overall zero net dipole. From Table 3.5, we can see that the (100), (011) and (111) are type III surfaces, which were therefore reconstructed through METADISE [134]to obtain a non-dipolar surface slab. In addition, the magnetic moments of Fe cations in the top layers decrease with respect to the 4.27 μ_B value simulated in the bulk, where the extent of the reduction is based on their reduced coordination number with the surrounding oxygen ions. For example, the fully-coordinated Fe cations in the (001) and (111) surface terminated with O have a larger magnetic moment (~4.22 μ B) than in the (110) surface (4.05 μ B), where only three oxygen ions are coordinating the Fe cations. Electrons remain in the undercoordinated Fe ion, thus causing the reduction of its magnetic moment.

Surface	Termination	Tasker type	Surface Energy (eV/nm ²)	<i>m_{sFe} (µ_B)</i> on top layer
001	0	II	5.27	4.22
010	O-Fe-O/O-Nb-O terminated	Π	1.97/4.41	4.10/-
100	Fe/Nb terminated	III	7.23/13.25	4.05/-
011	Fe/Nb terminated	III	3.47/7.51	4.13/4.15
101	O terminated	II	4.54	4.18
110	Nb-O-Fe/O terminated	II	3.32/4.02	4.19/4.19
111	O/Nb terminated	III	3.08/4.54	4.21/4.17

Table 3.5. Surface energy and magnetic moment for the low-Miller index surfaces of FeNbO₄ with the FM configuration,

The models of the simplest (001), (010) and (100) facets are shown in Figure 3.5. All slabs have the exposed atoms arranged regularly in the top and bottom layers. Nb and O form stronger bonds than Fe and O and, therefore, cleaving the surfaces with Nb in the top layers costs more energy than when Fe is in the top layers. For example, despite the Fe and Nb ions exposed in the top layer both having 3 dangling bonds in their two respective terminations of the (100) facet, the Nb termination has a larger surface energy of 13.25 eV/nm² compared to 7.23 eV/nm² for the Fe termination. Similarly, the (010) surface with the O-Fe-O termination has the lower energy of 1.97 eV/nm² and the lowest of the series of surface since there are only 2 dangling bonds per Fe atom whereas the O-Nb-O termination also with 2 dangling bonds per Nb atom has a higher surface energy of 4.41 eV/nm². These results also highlight the impact of the number of dangling bonds in the top layer on the surface energies.



Figure 3.5. Model of the (001), (010) and (100) FeNbO₄ surfaces and their energies: O atoms are in red; Fe atoms are in yellow and Nb atoms are in green.

In the more complex (011), (101), (110) and (111) surfaces, which are presented in Figure 3.6, the atomic configuration is less regular than in the previously discussed surfaces. In the (011) facet, although there is a similar atomic arrangement in the two different terminations if we ignore the type of metal cation type, the surface terminated with Fe cations has a much lower surface energy (3.47 eV/nm^2) than the Nb terminated surface (7.51 eV/nm^2) , since the Nb cations in the former plane have a larger coordination number than in the latter surface. This situation also occurs in the (111) facet, where there are more dangling bonds per Nb atom in the Nb termination (3.08 eV/nm²) than in the O termination one (4.54 eV/nm^2) , despite a similar atomic

arrangement. In addition, for the (101) facet there is only one surface type with a surface energy of 4.54 eV/nm² and although it has the same atom coordination as the (011) Fe termination, the latter's surface energy is remarkably larger, due to the loose arrangement of atoms in the (101) surface. Surprisingly, the O termination of the (110) facet has a higher surface energy (4.02 eV/nm^2) than the Nb-O-Fe termination (3.32 eV/nm^2), despite having fewer dangling bonds, which reflects the impact of the atomic arrangement on the surface energies. For example, we would suggest that the existence of the zig-zag FeO_x-NbO_x chains in the top layer could maintain the structural stability of the surface.

To summarize, the atomic arrangement, the type of cation and number of dangling bonds in the top layers all affect the surface energy, which is therefore difficult to predict. The (010) surface with O-Fe-O termination has the lowest surface energy (1.97 eV/nm^2) within this group of low-Miller index surfaces, since it has a tight arrangement of surface atoms and only a few Fe-O dangling bonds.



Figure 3.6. Model of the (011), (101), (110) and (111) FeNbO₄ surfaces and their energies: O atoms are in red; Fe atoms are in yellow and Nb atoms are in green.

Following the calculation of the surface energies and in order to explore which surfaces will be exposed in the nanoparticles of FeNbO₄ and have the potential to adsorb water, we constructed the Wulff morphology and calculated the STM images. Figure 3.7 shows the thermodynamic equilibrium crystal shape from the Wulff construction, which maintains the similar gem shape with the particles obtained by the flux method [154], and we are thus confident that our calculations are able to predict the correct relative surface stabilities. Figure 3.7 indicates that the main planes exposed in the nanoparticle are the (111), (110), (010) and (011) surfaces, with the (010) facet occupying the largest exposed area. As such, we only focus on these four major facets for the analysis of the STM images and the discussion of the water adsorption.



Figure 3.7. Different views of the equilibrium morphology of the FeNbO₄ crystal derived from a Wulff construction; a: vertical to <010> direction; b: side view.

Figure 3.8 shows the STM images of the FeNbO₄ (010), (011), (110) and (111) surfaces, where brightness represents height, *i.e.* the brighter the spot in the image, the closer is the ion to the STM probe tip. In the (010) surface, there is a distance of 1.30 Å between the topmost Nb and Fe ions, which are coordinated by four oxygen ions, two of which in the top layer and the other two in the sub-surface layer. The Fe ions lie above Nb and are therefore more exposed, making them good adsorption sites. In the (011) surface,

Fe is clearly located in the top layer and is coordinated by two oxygen ions also in the top layer. The atom density and arrangement in the (110) surface is less packed than in the other three surfaces, which led to atomic rearrangements during optimization. In the (111) surface, more Fe cations with one dangling bond are exposed than Nb cations, whereas the Fe ions in the sub-surface layers are partially covered by the surrounding oxygen ions from the top surface layer.



Figure 3.8. Calculated scanning tunnelling microscopy (STM) images of the (010), (011), (110) and (111) FeNbO₄ surfaces: O atoms are in red; Fe atoms are in yellow and Nb atoms are in green.

3.6 Adsorption and dissociation of water

In this section, we explore the adsorption of water, followed by its dissociation, at the Fe and Nb surface sites in the four main FeNbO₄ surfaces expressed in the morphology, *i.e.* (011), (010), (110) and (111).

3.6.1 Fe site

The optimized adsorption structures and energies at 0 K are shown in Figure 3.9. We can see that after optimization, the water molecules remain located above the Fe cations in both the (011) and (010) surfaces. In addition, the bond length between the interacting oxygen in water and the Fe ion in the top layer of the (011) surface (O_w -Fe) is the smallest (~2 Å) and closest to the Fe-O bond in the FeO₆ octahedron in the bulk of FeNbO₄. However, the O_w-Fe distance at the other three surfaces has a larger value of almost 2.2 Å. The largest adsorption energies of -1.02 and -0.82 eV were calculated at the (011) and (010) surfaces, respectively, which can be explained based on the adsorption configuration with the water interacting closely with the surfaces.

To provide further information on the molecular adsorption, we have also plotted the charge transfer by calculating the charge density difference ($\Delta \rho$) according to Eq (3-8):

$$\Delta \rho = \rho_{FeNbO_4 - H_2O} - \rho_{FeNbO_4} - \rho_{H_2O} \quad (3 - 8)$$

which is shown in Figure 3.9, where yellow colour represents charge depletion and blue colour represents charge gain. We found a clear charge transfer for all four surfaces with electron accumulation near the O_w -Fe bond, confirming the formation of this bond



during adsorption, which is also consistent with the adsorption energy analysis.

Figure 3.9. Most stable adsorption structures of H₂O on the Fe site of the FeNbO₄ (011), (010), (110) and (111) at 0 K (left) and the related charge density difference (right) where isosurface value is 0.003 e/bohr³: O atoms are in red; Fe atoms are in yellow and Nb atoms are in green.

We next analysed the dissociation reaction pathways of the water molecule on the same four surfaces at 0, 300 and 600 K, shown in Figures 3.10. The IS (initial state) represents the adsorption configuration where the surface-H₂O interface is formed. We found that all the adsorption free energies (ΔF_{ad}) presented by the gap between W+S and IS increase as the temperature rises, indicating that it becomes more difficult for a water molecule to attach to the surfaces, a process that becomes endothermic, indicating the contribution of vibration (ΔTS) can not be neglected at high temperature. Once adsorbed on the surfaces, the energy barriers from IS to TS are essentially the same on each surface for all temperatures. Specifically, in the mechanisms studied, the adsorbed water molecule dissociates to form surface-bound –H and –OH groups (final state: FS). On the (011) and (010) surfaces, we note a similar reaction path, where the bond between H and OH in the water molecule is broken and the H attaches itself to the nearest surface O in the top layer, with both adsorbate fragments binding the same FeO4 group. However, this reaction on the (010) surface has the largest free energy barrier $\Delta F_a = 2.6$ eV, showing that the dissociation reaction is more difficult and less likely to proceed on the (010) surface than on the other three surfaces. On the (111) surface, the dissociation reaction pathway involves the H atom bonding the nearest surface O anion in the neighbouring NbO₆ octahedron, with a barrier of 0.66 eV. On the (110) surface, a remarkable difference from the above three pathways is observed in the dissociation process. After adsorption of H_2O , the bridge between the FeO₄ and NbO₄ group in top layer is broken and the linking surface O anion moves towards its neighbouring Nb cation. As a result, each H atom from the water molecule forms a hydrogen-bond with the surface O anion that used to connect the FeO₄ and NbO₄ groups, with an activation energy of just 0.16 eV, *i.e.* the smallest barrier observed for the four surfaces at 0 K. During the dissociation process, the H atom from the water molecule coordinates the former bridging oxygen atom, which now belongs to the NbO₆ octahedron. We can conclude that owing to the migration of the bridging O anion in the top layer and the formation of the hydrogen-bonds during the dissociation process, the (110) surface displays the most favourable pathway with the smallest barrier. In summary, the dissociation process on the (010) surface requires the largest energy to overcome the activation energy barrier, and the reaction on the (110) surface is therefore the most likely process to occur, since it requires the smallest activation free energy $\Delta F_a = 0.16$ eV and the largest free energy for the dissociation reaction $\Delta F_{diss} = -0.52$ eV.



Figure 3.10. Water dissociation pathways in the FeNbO₄ (011), (010), (111) and (110) surfaces; W+S refers to isolated water molecule and surface; IS refers to initial state; TS refers to transition state; FS refers to final state.

3.6.2 Nb site

In this section, we investigated the reaction of a water molecule with the Nb cations in the top layer of the (011), (110) and (111) surfaces. Note that we did not consider this o_{re}

process on the (010) surface, since no Nb sites are exposed in the (010) surface. The adsorption structures after optimization at 0 K are shown in Figure 3.11, from which it is clear that on all three surfaces the bond distance between the water molecule and the Nb sites is longer than at the Fe sites discussed in the previous section. On both (011) and (111) surfaces, the exposed Nb cation coordinates five oxygen anions from the top surface layer and the dangling bond is used by the adsorbed water molecule, which has a similar position and distance of ~ 2.28 Å to the two facets. The adsorption energy of a water molecule binding to the (011) surface is -0.87 eV at 0 K, which is smaller than at the Fe site (-1.02 eV). Note that Nb has a larger Bader charge and we therefore should expect the interaction between Nb and O to be stronger than between Fe and O. However, we consider that these unexpectedly lower adsorption energies are caused by steric effects at the adsorption sites from the neighbouring atoms. For example, despite both Fe and Nb having six-fold bulk coordination, the Fe cation in the (011) surface is coordinated by only four oxygen anions, making it a more available adsorption site than the Nb cation, which has a coordination number of five and is therefore less accessible for molecular adsorption. Moreover, for a similar arrangement of the surface O near the adsorption site, we found that the adsorption energy released at the Nb site is 0.02 and 0.78 eV larger than at the Fe site of the (110) and (111) surfaces at 0 K, respectively, despite the longer Nb-O bond distance compared to the Fe-O interaction. To gain further insight into the interaction mechanism, we next calculated the charge transfers between the water molecules and surfaces, shown in Figure 3.11. Similar to the result at the Fe site, we found charge transfers between all the three surfaces and the water molecules,





Figure 3.11. Most stable adsorption structures of H₂O on the Nb site of the FeNbO₄ (011), (110) and (111 at 0 K and the related charge density difference where isosurface value is 0.003 e/bohr³: O atoms are in red; Fe atoms are in yellow and Nb atoms are in green.

Finally, we calculated the water dissociation pathways at the Nb site on the three surfaces, which are shown in Figure 3.12. Similar to the reactions on Fe site, our simulations also suggest that the adsorption free energies (ΔF_{ad}) from W+S to IS becomes positive with the increment of temperature and after water dissociation the H migrates and attaches to the nearest O in the top surface layer. We also found that during water dissociation on the (110) surface, the system only needs to overcome a very small activation energy barrier of 0.27 eV at 0 k, compared to a barrier of 0.82 eV on the (011) surface and 0.36 eV on the (111) surface. Our calculations indicate that the water dissociation reaction on the (110) surface releases 0.43 eV of energy at 0 K, whereas this process on the other two surfaces is endothermic, requiring 0.53 eV and 0.11 eV, respectively. Unlike the process at the Fe site, the dissociation pathway at the Nb site on the (110) surface, does not induce the migration of the bridging O towards the Nb cation. In summary, the water dissociation reaction at the Nb site of the (110) surface is the most easily achieved with the smallest activation free energy value $\Delta F_a = 0.27$ eV and the largest free energy for the dissociation reaction $\Delta F_{diss} = -0.43$ eV.



Figure 3.12. Water dissociation pathway in the FeNbO4 (011), (110) and (111) surface; W+S refers to isolated water molecule and surface; IS refers to initial state; TS refers to transition state; FS refers to final state.

3.7 Chapter conclusion

In this chapter, we have carried out a comprehensive computational study of the bulk and surface properties of the monoclinic phase of FeNbO₄, including the adsorption and dissociation reaction of water on its surfaces. The optimized bulk structure shows a typical monoclinic lattice with a unique axis b (β =90.4°) where the Fe cations stay in a high spin state with a magnetization of 4.27 µ_B. The Bader charge of the Nb cations is larger than for the Fe atoms, which explains the stronger Nb-O bond compared to the Fe-O bond. The PDOS plot explains that the electron conduction takes place through the Fe-O-Fe sub-lattice, which is consistent with the experimental results. The calculated elastic constants meet all the stability conditions for the monoclinic phase. The (010) facet has the lowest surface energy and occupies the largest area in the Wulff construction morphology, where the (011), (110) and (111) facets are also exposed. The surfaces terminated with Nb cations with four- or three-fold oxygen coordination have the largest surface energy, owing to the strong Nb-O bond.

Finally, we studied the adsorption and dissociation reaction of a water molecule at the Fe and Nb sites exposed in the four surfaces expressed in the morphology. For all surfaces, the adsorption reaction will become endothermic with the increment of Temperature and, the most favourable water adsorption takes place at the Nb site of the (111) surface and at the Fe site of the (011) surface, releasing adsorption energies of - 1.17 and -1.00 eV, respectively. The dissociation of water at both the Fe and Nb sites could be achieved most easily on the (110) surface, which also displays the lowest activation energy barriers at 0 K, supporting the feasibility of this process.

Chapter 4: Dissociation of hydrogen on the surfaces of o-FeNbO₄

4.1 Abstract

The o-FeNbO₄, where the Fe and Nb cations are distributed randomly in the octahedral 4c site, has shown excellent promise as an anode material in solid oxide fuel cells. In this chapter, we have used DFT+U-D2 method to explore the adsorption and dissociation of H₂ molecules and the formation reaction of water at the surfaces. We have generated pristine surfaces with random distributions of cations from a 2×2×2 quasi-random orthorhombic bulk structure. Specifically, we have considered various terminations for the (010) and (111) surfaces with different ratios of Fe and Nb cations in the exposed layers. The top and sub-surface layers of the (010) surface move in opposite directions after relaxation, whereas the relaxed layers of the (111) surface shift outward by no more than 2.5%. Simulations of the surface properties confirmed that the bandgaps are reduced to less than 0.5 eV. We found that the hydrogen molecule prefers to dissociate at the O bridge sites of the (010) and (111) surfaces, especially where these are coordinated to Fe cations, thereby forming two hydroxyl groups. We have investigated the water formation reaction and found that the energy barriers for migration of the H ions are generally lower for the Fe/Nb-O sites than for the O-O site.

Overall, our simulations predict that after dissociation the H atoms tend to remain stable in the form of OH groups, whereas a larger barrier needs to be overcome to achieve the formation of water. Future work will focus on modifying the surfaces to reduce further the barrier of migration of the dissociated H ions, especially from the oxygen bridge sites.

4.2 Introduction

Since the beginning of the 21st century, climate change and air pollution have become a global crisis that affects the whole of society. One way to reduce the risk of escalation is to deploy alternative green energy sources, like hydrogen, to replace traditional fossil fuel sources. Hydrogen is considered as one of the most promising sources to achieve a sustainable energy future, due to its abundant reserves in the form of water and renewability.[40-45]

SOFCs, which consist of all solid-state cathode, electrolyte and anode, are devices of particular interest, since they have high efficacy and the ability to process different fuels, including hydrogen, hydrocarbons and carbon monoxide, under medium and high temperatures (above 700 °C) to produce electricity.[40-42] At the anode, the reaction takes place where fuel gases are oxidized to CO₂ or H₂O, providing electrons to the external circuit. Over the past years, Ni metal has been considered a good anode material, owing to its low cost, good catalytic ability and high electronic conductivity.[50-52, 61, 155-163] However, Ni-metal anodes have shown poor

tolerance to sulfur and carbon deposition, [41, 42, 44, 45] which limits the chemical activity under long-term operation. As a result, several alternative ceramic materials, such as CeO₂ and La_{0.75}Sr_{0.25}CrO₃ (LSCr), have been developed to replace Ni metal as the anode material in SOFCs.[65-67, 164-166] Those oxide anode materials offer resistance to carbon deposition and stability during the operation of SOFCs at high temperatures, but they show lower catalytic efficiency and electronic conductivity than Ni-metal anodes.

In addition to the CeO₂ and LSCr anode materials, research on Fe-based materials, *i.e.* LaFeO₃, FeVO₄, and FeNbO₄, has also made significant progress.[117-119, 167, 168] For example, previous studies have shown that orthorhombic FeNbO₄ materials are good catalysts for hydrogen dissociation above 700 °C, where Nb⁵⁺ cations remain stable while Fe³⁺ cations are reduced to Fe²⁺ under H₂ atmosphere. In contrast to many other Fe-based oxides, the Fe and Nb cations are distributed randomly in the orthorhombic structure (o-FeNbO₄) and thus layers consisting of only Fe³⁺ cations do not exist, see Figure 4.1. Furthermore, the random distribution of Fe³⁺-Fe²⁺ chains throughout the whole material under operation ensures that the electrons can be conducted along the 3D Fe-O-Fe network and the continuous reduction of Fe³⁺ in the same layer can be avoided, which explains why the o-FeNbO₄ phase has good structural stability and relatively high electronic conductivity.[10]

The reaction mechanism of the oxidation of fuels, especially hydrogen, at the surfaces of o-FeNbO₄ is not as yet well understood. In this chapter, we have selected the (010) and (111) surfaces of o-FeNbO₄, which were shown to be the major pristine surfaces in

the previous chapter to explore their activity towards the H_2 molecule. Random distributions of cations and different stacking sequences of the surfaces have been considered to simulate realistic o-FeNbO₄ configurations. We have used calculations based on the DFT+*U*-D2 method to study the surface properties and reactions with the H_2 molecule, including the dissociation of H_2 , diffusion of H atoms and water formation.

4.3 Computational method

In this chapter, the Vienna Ab initio Simulation Package, VASP (version 5.4.4), has been employed to carry out the DFT calculations.[126-129] In all calculations, the ionelectron interactions were described by the projector-augmented wave method (PAW).[96] The following electrons were treated as valence electrons: Fe ($3p^63d^74s^1$), Nb ($4p^65s^{1}4d^44s^2$), O ($2s^22p^4$) and H ($1s^1$). We have employed the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) functional to perform all spin-polarized simulations.[130] To enhance the electronic structures, the on-site Coulombic interaction (DFT+U) introduced by Dudarev *et al.* [90] was chosen for the Fe 3d electrons with a U_{eff} value of 4.3 eV.[131, 132] The kinetic energy cutoff for the plane waves was set at 500 eV and all calculations were performed using the tetrahedron method with Blöchl corrections. The Henkelman algorithm was used to calculate Bader charges.[133] A 2×2×2 supercell with random distributions of cations and a spin-glass phase, comprising 16 Fe, 16 Nb and 64 O (Figure 4.1), was obtained via the special quasi-random structures (SOS) method, which is based on a Monte Carlo simulated annealing loop with an objective function designed to perfectly match the maximum number of correlations.[169] This method is implemented in the Alloy Theoretic Automated Toolkit (ATAT).[170-172] Specifically, Fe₅Nb₃, Fe₃Nb₅, Fe₃Nb₅ and Fe₅Nb₃ were distributed alternatively along a direction in the $2 \times 2 \times 2$ supercell. We have used the METADISE code [134] to create the dipolar (010) and (111) surfaces from the $2 \times 2 \times 2$ supercell. In addition, $3 \times 3 \times 3$, $2 \times 2 \times 1$ and $3 \times 3 \times 3$ gamma centered Monkhorst Pack grids were used for the simulation of the bulk, surface slabs, and isolated hydrogen/water molecule in a 10 Å \times 10 Å \times 10 Å cubic box, respectively. All calculations of the surface and bulk were carried out with the DFT-D2 method implemented in VASP to incorporate the Van der Waals correction.[98] In terms of the optimization of the surfaces, we fixed the bottom 50% of atomic layers at their relaxed bulk positions, whereas the top 50% were allowed to relax unconstrainedly to obtain the optimized surfaces. The Bader charges and magnetic moments of the surface atoms are calculated using an improved grid-based algorithm and the work function is obtained using the following equation:

$$\Phi = E_{vac} - E_F \quad (4-1)$$

where E_{vac} is the vacuum level and E_F is the Fermi level of the surfaces.



Figure 4.1. 2×2×2 supercell of the orthorhombic FeNbO₄ structure obtained from the ATAT model; O atoms are red; Fe atoms are yellow; Nb atoms are green.

In addition, all geometry optimizations in this chapter were performed with the conjugate gradient method with a convergence criteria of 0.01 eV/Å. We employed the climbing image nudge elastic band (CI-NEB) method [139] to study the transition states of the migration of H ions. For transition states, we inserted five consecutive images along the minimum energy path (MEP) from the dissociation of hydrogen to the formation of water to calculate saddle points, where the calculations were carried out using the limited memory Broyden Fletcher Goldfarb Shanno (LBFGS) method [140] until the forces were smaller than 0.05 eV/Å. We confirmed that each transition state has an imaginary vibrational frequency along the reaction direction.

The Helmholtz free energy of the dissociation process of H₂ was calculated using:

$$\Delta F = \Delta E + \Delta E_{ZPE} - T\Delta S \quad (4-2)$$

where ΔE , ΔE_{ZPE} , and ΔS are the variation of electronic energy obtained from the DFT calculations, the zero-point energy correction, and the vibrational contribution to

entropy, respectively. In this chapter, ΔE_{ZPE} and ΔS were obtained by calculating vibrational frequencies via the VASPKIT code.[173] The experimental entropy ΔS for gaseous H₂ was obtained from the NIST database.[142]

The energy for the adsorption of H₂ can be expressed as:

$$\Delta E = E_{sur+H_2} - E_{sur} - E_{H_2} \quad (4-3)$$

where E_{sur+H_2} represents the total energy of surface-H₂, E_{sur} represents the total energy of the pristine surface and E_{H_2} represents the energy of the isolated H₂ molecule.

4.4 Surface properties

We know from the previous chapter that the (010) and (111) surfaces with the FM configuration are the two dominant surfaces of FeNbO₄. In this chapter, we have created simulation cells of 8 layers for the (010) surfaces and 4 layers for the (111) surface, see Figures 4.2 and 4.3. The (010) surfaces were stacked with the sequence of $-Fe_3NbO_8$ - $Fe_2Nb_2O_8$ - $FeNb_3O_8$ -, whereas the (111) surfaces show the order of $-Fe_8Nb_8O_{32}$ - $Fe_8Nb_8O_{32}$ - along the z axis. In addition, we found that the exposed cations in the topmost layers of the (010) surfaces are coordinated by four oxygen atoms, forming two dangling bonds towards the vacuum. Thus, there appear three terminations for the (010) surface, *i.e.* the (FeO₄)₃(NbO₄)₁- , the (FeO₄)₂(NbO₄)₂- and the (FeO₄)₁(NbO₄)₃-terminations, which are renamed as Fe_3Nb_1 -, Fe_2Nb_2 - and Fe_1Nb_3 -terminations, respectively in the following discussion.



Figure 4.2. Side view (a-c) and top view (d-e) of the three (010) surfaces and their corresponding stacking sequences; O atoms are in red; Fe atoms are in yellow; Nb atoms are in green.

However, each later in the (111) surface comprises the same number of cations and we have therefore only selected one termination to explore its surface properties and reactions with the H₂ molecule. It is worth noting that in the top layers the two Fe and two Nb cations are in fully coordinated by oxygen, whereas the other six Fe and six Nb are five-fold coordinated cations, leading to one dangling bond each towards the Figure 4.3. From here will denote the vacuum, see we on, (FeO₅)₆(FeO₆)₂(NbO₅)₆(NbO₆)₂-termination as Fe₈Nb₈.



Figure 4.3. Side view (a) and top view (b) of the (111) surfaces and their corresponding stacking sequences; the black ellipse refers to the Fe/NbO₆; O atoms are in red; Fe atoms are in yellow; Nb atoms are in green.

First, we have calculated the Bader charges, magnetic moments and work functions of the four surfaces, listed in Table 4.1, where the Bader charges and magnetic moments of the surface models are the average values of the exposed ions. Our simulations show that the Bader charge of the fully coordinated Fe cations in the bulk model is larger than that of the Fe cations with dangling bonds in the surfaces. Similar trends can be found for the Bader charges of the Nb and O ions, *i.e.* the Bader charges of the exposed ions are slightly smaller than those in the bulk structure. The magnetic moment of the Fe cations in the bulk is $4.21 \mu_B$, which is reduced to 4.18, 4.16, 4.15 and $4.19 \mu_B$ for the Fe₃Nb₁-, Fe₂Nb₂-, Fe₁Nb₃- and Fe₈Nb₈-terminated surfaces, respectively. We found that the Nb and O ions in both the bulk and surface models have zero magnetic moments. The calculated work function of the F₁N₃-terminated (010) surface is 7.29 eV, which is significantly larger than the other three terminations.

In general, our simulations indicate that the Bader charges and the magnetic moments of the exposed ions are related to the coordination numbers. For instance, the Fe and Nb cations with one dangling bond have larger values of q and m_s than those with two dangling bonds, indicating that the five-fold cations, especially the Fe in the (111) surface, are in a higher oxidation state than the four-fold cations on the (010) surfaces. In addition, we found that the work functions of the (010) surfaces are generally smaller than that of the (111) surface, with the exception of the Fe₁Nb₃-terminated (010) surface, suggesting that the number of exposed Nb cations can negatively affect the surface reactivity. Whereas, we did not calculated the surface energies of those surfaces due to the structural asymmetry.

Table 4.1. Average Bader charge (q) and the average magnetic moment (m_s) of the ions on the top layers and the work function.

	<i>q</i> Fe(e)	<i>q</i> _{Nb} (e)	<i>q</i> o(e)	<i>ms</i> Fe(µB)	<i>ms</i> Nb(µB)	<i>ms</i> o(µB)	Ф (eV)
Bulk	+1.84	+2.71	-1.14	4.21	0	0	-
Fe3Nb1-Termination	+1.76	+2.62	-1.06	4.18	0	0	5.44
Fe2Nb2-Termination	+1.75	+2.62	-1.06	4.16	0	0	5.13
Fe1Nb3-Termination	+1.73	+2.59	-1.04	4.15	0	0	7.29
Fe ₈ Nb ₈ -Termination	+1.79	+2.63	-1.03	4.19	0	0	6.02

Figure 4.4 shows the interplanar distances of the three (010) and the (111) surfaces, which were defined as $\Delta_{ij} = 100(d_{ij} - d_{ij}^{\circ})/d_{ij}^{\circ}$, where d_{ij} and d_{ij}° are the distance between the relaxed i and j = i+1 layers in the surface and bulk models, respectively. As mentioned above, the Fe₃Nb₁-, Fe₂Nb₂- and Fe₁Nb₃-terminated surfaces contain eight layers, namely FeNbO-1 to FeNbO-8, whereas four layers constitute the (111) surface model and we therefore only plotted the data from FeNbO-1 to FeNbO-4. Our simulations suggest that after relaxation the topmost layer FeNbO-1 of the three (010) surfaces moves towards bulk by 6.7 %, 8.71 % and 0.55 % in the Fe₃Nb₁-, Fe₂Nb₂- and Fe₁Nb₃-terminated surfaces, respectively. The subsequent layers from FeNbO-2 to FeNbO-4 experienced gradually decreased relaxation outwards from the bulk from 6.4 to 1.7% and 5 to 0.5% for the Fe₃Nb₁- and Fe₂Nb₂-terminated surfaces, respectively, whereas the Fe₁Nb₃-terminated surface suffered the maximum relaxation of 3.6% outwards from the bulk in the FeNbO-3 layer. For the Fe₈Nb₈-terminated surface we found that the topmost FeNbO-1 layer shifts outwards by 2.5% which trend decreased to 0.55% for the sub-FeNbO-2 layer. Overall, our calculations indicate that the relaxation of the FeNbO-1 and FeNbO-2 layers shows a contradictory tendency and thus, those two layers tend to merge to form the exposed side. In contrast, we found that both the two relaxed layers of the (111) surface move outward from the bulk by no more than 2.5%.



Figure 4.4. Interplanar distances of the four surfaces.

Next, we simulated the PDOS of the four surfaces, see Figure 4.5. The localized t_{2g} and e_g orbitals of the Fe ions near -8 eV are distributed over both the major and minor spin

channels on the four surfaces, whereas the 3d states of Nb and 2p states of O are delocalized in the wide valence region from -8 to 0 eV. The unoccupied conduction region is mainly composed by the d states of the metal cations at those surfaces. In addition, our simulations indicate that in the (010) surfaces, the band gap decreases with the numbers of exposed four-fold Fe cations, suggesting the sequence: $E_{bandgap}^{Fe2Nb2} < E_{bandgap}^{Fe1Nb3}$. In contrast to the (010) surfaces, the Fermi level of the (111) surface is located at the midpoint between VBM and CBM, reducing the band gap to 0.3 eV. Overall, we found that the DOS of the surfaces display a different distribution and the bandgaps are significantly reduced compared to the bulk model material elucidated in our previous chapter, because the existing metal-oxygen dangling bonds in the exposed surface layers can behave as chemically active sites, which is also found in other studies.[73, 75, 174, 175]



Figure 4.5. Projected density of states (PDOS) of FeNbO₄ of the surfaces: (a) Fe₃Nb₁-termination; (b) Fe₂Nb₂-termination; (c) Fe₁Nb₃-termination; (d) Fe₈Nb₈-termination;

The STM images, which are generated at a bias of -3.5 eV, are plotted in Figure 4.6. We found that the brightest spots represent the oxygen atoms, whereas the cations cannot be identified very well owing to their low resolution. The presence of cations from the sub-surface layers can be seen on the (010) surfaces, in agreement with the analysis of the interplanar distance. In addition, our simulations suggest that the array of O-Fe/Nb-O-Fe/Nb appears along the $[\overline{1}0\overline{1}]$ direction on the (010) surfaces, and similarly the five-fold Fe/Nb cations are distributed along the $[\overline{1}10]$ direction on the (111) surface.



Figure 4.6. Calculated scanning tunneling microscopy (STM) images of the surfaces: (a) Fe₃Nb₁-termination; (b) Fe₂Nb₂-termination; (c) Fe₁Nb₃-termination; (d) Fe₈Nb₈-termination; O atoms are in red; Fe atoms are in yellow; Nb atoms are in green.

4.5 Dissociation of H₂

In a real disordered orthorhombic FeNbO₄ structure, it is believed that the dissociation reactions of hydrogen take place at the surfaces, where Fe and Nb cations distribute randomly. In this chapter, the four generated surfaces display random distributions of cations on a 2×2 scale. To explore the mechanisms of surface reactions, we have only introduced one hydrogen molecule and placed it in different sites to investigate how the surface ions affect the dissociation reactions.

4.5.1 (010) surface

As shown, the Fe/Nb cations are coordinated by four oxygen ions in the exposed layers of the (010) surfaces. We identified three types of surface moieties, *i.e.* Fe-O-Fe, Fe-O-Nb and Nb-O-Nb, creating six O-O dissociation sites, which are represented by $O_{FeFe-FeFe}$, $O_{FeFe-FeNb}$, $O_{FeFe-NbNb}$, $O_{FeNb-FeNb}$, $O_{NbNb-FeNb}$ and $O_{NbNb-NbNb}$, respectively, see Figure 4.7. It worth noting that we did not consider the $O_{NbNb-NbNb}$, $O_{NbNb-NbNb}$, and $O_{FeFe-FeFe}$ sites on the Fe₃Nb₁- Fe₂Nb₂- and Fe₁Nb₃-terminated surfaces, respectively, owing to the lack of Nb and Fe cations in the top and sub-surface layers.



Figure 4.7. Fe/Nb-O dissociation sites (a-c) and O-O sites (d-f) of the (010) surfaces; (a,d) Fe₃Nb₁-termination; (b,e) Fe₂Nb₂-termination; (c,f) Fe₁Nb₃-termination; (d) Fe₈Nb₈-termination; O atoms are in red; Fe atoms are in yellow; Nb atoms are in green.

First, we have calculated the dissociation energies at all sites on the surfaces from 0 to 900 K, see Figure 4.8. Our simulations show that the dissociation of H₂ at the $O_{FeFe-FeFe}$ and $O_{FeFe-FeNb}$ sites of Fe₃Nb₁- and Fe₂Nb₂-terminated surfaces remain energetically favorable from 0 to 900 K, whereas the reactions at other sites, *i.e.* the Fe - O, Nb - O, $O_{FeFe-NbNb}$, $O_{FeNb-FeNb}$, and $O_{NbNb-FeNb}$ sites, turns into endothermic processes as the temperature is raised. Especially, we found that the dissociation at the $O_{NbNb-FeNb}$ sites are significantly endothermic even at 0 K. On the Fe₁Nb₃-terminated surface the $O_{FeFe-FeNb}$ and $O_{FeFe-NbNb}$ are the two thermodynamically favorable sites between 0 to 900 K, with the dissociation energy ranging from -1.96 to -1.57 eV and -1.54 to -0.18 eV, respectively, whereas the reactions at the $O_{FeNb-FeNb}$, $O_{NbNb-FeNb}$, $O_{NbNb-NbNb}$, Fe - O and Nb - O sites become endothermic from 900 K, 600 K, 600 K, 300 K and 0 K, respectively. Overall, our simulations indicate that the dissociation energies on all the surfaces increase with temperature and the energies on the F_3N_1 - and F_2N_2 -terminated surfaces show the same $E_{NbNb-NbFe} < E_{Nb-O} < E_{Fe-O}, < E_{FeFe-NbNb} < E_{FeNb-FeNb} <$ order of $E_{FeFe-FeNb} < E_{FeFe-FeFe}$, whereas the order changes into $E_{Nb-O} < E_{Fe-O} <$ $E_{NbNb-NbNb} < E_{FeNb-FeNb} < E_{NbNb-FeNb} < E_{FeFe-NbNb} < E_{FeFe-FeNb}$ on the Fe₁Nb₃-terminated surface. Interestingly, on the one hand we found that the number of Fe cations coordinated to the O sites can affect the dissociation energy. For instance, the H₂ molecule prefers to be dissociated at the $O_{FeFe-FeFe}$ and $O_{FeFe-FeNb}$ sites, with respect to the $O_{NbNb-NbNb}$ and $O_{NbNb-NbFe}$ sites. On the other hand, however, the dissociation energies at the $O_{FeFe-FeFe}$ and $O_{FeFe-FeNb}$ sites of the three surfaces





Figure 4.8. Dissociation energy of H₂ on the (010) surfaces from 0 to 900 K.

In previous work, [72-76] the dissociation of the hydrogen molecule at the O sites has been studied extensively and H atoms coordinated by oxygen are generally oxidized after dissociation. To explore how the electrons are transferred at the metal-oxygen sites in this chapter, we have focused on the charge transfer difference and other properties, *i.e.* Bader charge and bond length, at the Fe/Nb-O sites, see Figure 9. Our simulations suggest that the H atoms from the O-H and the Fe/Nb-H groups are surrounded by electron depletion and gain areas, respectively. Correspondingly, a relatively small gain and depletion area is distributed around the O and Fe/Nb atoms, respectively. We found that the electron depletion area around the hydroxyl at the Nb-O site is slightly larger than that at the Fe-O site. The calculated Bader charge of the H for the hydroxyl ranges from +0.60 to +0.67, whereas the H atoms coordinated by Fe have Bader charges of -0.19 to -0.29, which is smaller than those bound to Nb. In addition, we have shown the bond lengths in Figure 4.9, where the Fe-H bond at 1.79 Å is slightly longer than the Nb-O bond (1.76 Å) on the Fe₃Nb₁-terminated surface. In contrast, in the Fe₂Nb₂- and Fe₁Nb₃-terminated surfaces, the Nb-O bond length is longer than that of Fe-O, because on the Fe₃Nb₁-terminated surface the Fe cation in the sub-surface layer exhibits similar chemical activity towards the dissociated H atom, which therefore tends to move closer to this Fe atom at a distance of 1.91 Å after optimization. A O-H bond length of approximately 0.98 Å was obtained in all the hydroxyl groups. Overall, our simulations demonstrated that after dissociation at the metal-oxygen sites, one H atom becomes bonded tightly to the oxygen, forming a hydroxyl group, whereas another H atom is captured by the surrounding metal cations, forming the relatively weak Fe/Nb-H bond. In this process, electrons are transferred from one dissociated H atom to the coordinated O atom, whereas the other H atom obtains electron from the metal side.


Figure 4.9. Charge transfer difference at the (a-c) Fe-O and (d-f) Nb-O sites of the (010) surfaces after dissociation of H₂; (a,d) Fe₃Nb₁-termination; (b,e) Fe₂Nb₂-termination; (c,f) Fe₁Nb₃-termination; (d) Fe₈Nb₈-termination; the isosurface value is 0.002 e/bohr³; O atoms are in red; Fe atoms are in yellow; Nb atoms are in green; H atoms are in white.

4.5.2 (111) surface

On the (111) surface, we found that five-fold cations are exposed in the top layers and thus, we have taken into account the seven adsorption sites which includes two metaloxygen sites, which are similar to the (010) surfaces, and five oxygen-oxygen sites, see Figure. Specifically, for the oxygen-oxygen sites, the $O_{Fe/Nb}$ denotes the site where the two oxygen are coordinated by one five-fold cation, whereas in another type of reaction site, *i.e.* O_{Fe-Fe} , O_{Fe-Nb} and O_{Nb-Nb} , the two oxygen atoms are shared by two square pyramids, see Figure 4.10.



Figure 4.10. Dissociation sites of H₂ on the (111) surface; O atoms are in red; Fe atoms are in yellow; Nb atoms are in green.

Figure 4.11 shows the dissociation reaction energy at the (111) surface under different temperatures. We found that the reactions at the O_{Fe} site are much more thermodynamically favorable than at the other three sites, and especially the dissociation energies remain negative from 0 to 900 K, even larger than was found for W-doped Al₂O₃ and WO_x materials.[174, 175] At another oxygen site, *i.e.* the O_{Nb} site, the dissociation reaction is exothermic by -1.74 eV at 0 K but increases to ~0 eV when the temperature reaches 900 K. At the other sites, the reactions gradually become endothermic as the temperature increases, with the exception of the O_{Fe-Nb} site, where the dissociation energy is positive from 0 K upwards. In general, our simulations indicate that the O_{Fe} site is the most thermodynamically favorable site on the (111) surface, and the priority of the reaction occurs in the sequence : $E_{O_{Fe-Fe}} < E_{Nb-O} < E_{O_{Nb-Nb}} < E_{O_{Fe-Fe}} < E_{Fe-O} < E_{O_{Nb}} < E_{O_{Fe}}$. In addition, we found that the oxygen sites on the (111) surface have similar chemical activity to those on the (010) surfaces,

whereas the Fe/Nb-O sites on the (111) surface are more active than on the (010) surfaces, suggesting that the five-fold cations exposed in the top layer play a more important role in the dissociation of H_2 than the four-fold cations.



Figure 4.11. Dissociation energy of H₂ on the F₈N₈-terminated surface from 0 to 900 K.

The charge transfer difference at the Fe/Nb-O sites is plotted in Figure 4.12. Our simulations suggest partial electronic density transfer from the cations to hydrogen at the Fe/Nb-O site and from hydrogen to oxygen at the O-H site, similar to the change of electronic distribution in the (010) surfaces. In addition, we found that the electron gain area around the Nb site is larger than that around the Fe site, in agreement with the larger Bader charge of -0.39 e for the H coordinated by Nb. The bond lengths of the hydroxyls are close to 0.98 Å, whereas the Fe- and Nb-H bonds at the Fe/Nb-O site are longer than the O-H by 0.58 and 0.82 Å, respectively. Compared with the (010) surfaces, we found that the differences in the charge transfer, Bader charge and the bond length of the metal/oxygen-H between the (010) and (111) surfaces are small, with the

exception of the Fe-O site of the (111) surface where the H coordinated by Fe has the smallest Bader charge of -0.16 e and the Fe-H has the shortest bond length at 1.56 Å.



Figure 4.12. Charge transfer difference at the (a) Fe-O and (b) Nb-O sites of the (111) surface after dissociation of H₂; the isosurface value is 0.002 e/bohr³; O atoms are in red; Fe atoms are in yellow; Nb atoms are in green; H atoms are in white.

4.6 Formation of water

The dissociation process of hydrogen at the surfaces revealed above shows that the formation of water can take place at both the Fe/Nb-O and O-O sites. To gain a relatively full insight into the mechanism, we have chosen the Fe-O sites of the (010) surfaces and the the O_{Fe} site of the (111) surface to simulate the migration pathways of dissociated H atoms and the water formation reactions. After dissociation on the (010) surfaces, the H atoms coordinated with the Fe cations migrate towards the nearby oxygen ions to form a H₂O molecule, which then desorbs from the surfaces, forming an oxygen vacancy in the top layer, which in the SOFCs process will be filled again by the oxygen ions from electrolyte. The proposed reaction process is shown in Figure 4.13.



Figure 4.13. Pathways of the water formation reaction on the (010) surface (top) and the (111) surface (bottom); O_v refers to oxygen vacancy.

Figure 4.14 shows the hydrogen migration at the surfaces after dissociated on the top layers. Our simulations show that the H₂O molecule is not stable on the Fe₃Nb₁terminated surface. Instead, one H atom tends to be captured by the adjacent oxygen ion, forming a hydrogen-bond, leading to the two top O ions from the hydroxyl groups getting close to each other within a distance of 2.7 Å. In contrast, we found that the H₂O molecules are stable on both the Fe₂Nb₂- and Fe₁Nb₃- terminated surfaces, where the bond length of the nearby metal-oxygen on the Fe₁Nb₃- terminated surface is longer by 0.3 Å compared to the Fe₂Nb₂-terminated surface. In addition, we found that the longest bond distance of 3.12 Å is the (H)O(H)--Fe bond on the Fe₈Nb₈-terminated (111) surface. Overall, our calculations suggest that the bound H₂O molecules are generally stable on the surfaces, with the exception of the Fe₃Nb₁-terminated surface. These water molecules could leave the surfaces, as evidenced by the lengthening of the metaloxygen bonds compared to those in the bulk structure.[176] We would suggest that the H atoms on the Fe₃Nb₁-terminated (Fe-rich) surface prefer to form two hydroxyl groups could be partially due to the oxygen ions in the Fe-rich region having a similar chemical activity towards the dissociated H atoms.



Figure 4.14. Optimized structures after the diffusion of H atoms on the four surfaces; (a) Fe-O site of the Fe₃N_{1b}-terminated (010) surface; (b) Fe-O site of the Fe₂Nb₂-terminated surface; (c) Fe-O site of the Fe₁Nb₃-terminated surface ;(d) O_{Fe} site of the Fe₈Nb₈-terminated surface; O atoms are in red; Fe atoms are in yellow; Nb atoms are in green; H atoms are in white.

The energy pathways are plotted in Figure 4.15. Our calculations show that the energy barriers from the dissociated *2H to the adsorbed H₂O* states are in the range of 0.44 to 0.54 eV on the three (010) surfaces, compared to 1.08 eV on the Fe₈Nb₈-terminated (111) surface, which is still much lower than the migration barrier of 3.53 eV reported for the pure CeO₂ system.[75] In addition, the formation of the surface-bound water molecules is an energetically favourable process on the (010) surfaces, although on the (111) surface, the energy of the H₂O* state is similar to that of the *2H state. Finally, the desorption from the surfaces into a gaseous water molecule is also calculated, which is represented by the process from the H₂O* to the H₂O (g) state. The lowest barrier (1.02 eV) is found for the (111) surface, which is larger than the barrier in the Ni-YSZ anode (0.6 eV) but close to the CeO₂ materials (0.9 eV).[75, 177] Overall, our simulations indicate that migration of the dissociated H atoms on the (111) surface

needs to overcome a larger barrier than on the (010) surfaces to form the surface-bound water molecules, which can be explained by the fact that the O-H bond is stronger than the Fe-O, in agreement with the analysis of the Bader charges. In addition, we found that water formation on the Fe₃Nb₁-terminated surface is more endothermic than on other surfaces, indicating that forming gaseous water molecules though two hydroxyl groups is energetically difficult compared to the directly bonded water molecules.



Figure 4.15. Energy pathways of diffusion of H and water formation on the four surfaces; 2H* refers to the dissociation of H₂; TS refers to the transition state from H₂ dissociation to H₂O; H₂O* refers to the adsorbed H₂O and H₂O (gas) refers to the desorption of H₂O.

4.7 Chapter conclusion

In this chapter, we have employed DFT+U-D2 calculations to investigate the surface properties of the o-FeNbO₄ material, the adsorption and dissociation of H₂ molecules,

the migration of H ions, as well as the formation of water at the (010) and (111) surfaces. First, the calculations of the surface properties have demonstrated that the five-fold cations in the (111) surface show a higher oxidation state than the four-fold cations in the (010) surfaces, and the bandgaps of those surfaces are reduced to less than 0.5 eV. The simulated interplanar distances indicate that the first two top layers of the three (010) surfaces move in opposite directions, leading to the metal cations in the subsurface layers becoming exposed to the vacuum, whereas the relaxed two layers of the (111) surface shift outwards from the bulk. We have selected the Fe/Nb-O and O-O sites on the (010) and (111) surfaces as the dissociation sites for the H₂ molecule. At the Fe/Nb-O sites, the five-fold cations of the (111) surface enable dissociation more than the four-fold Fe/Nb in the (010) surfaces. In addition, our calculations indicate that the numbers of Fe cations coordinated to the O can affect the dissociation energies. Specifically, dissociation at the $O_{FeFe-FeFe}$ and $O_{FeFe-FeNb}$ sites of the (010) surfaces remain exothermic from 0 to 900 k, whereas the reaction at other sites becomes endothermic at temperatures below 900 K. Similarly, we found that the hydrogen molecule prefers to dissociate at the O_{Fe} site of the (111) surface, where the reactions remain exothermic in the range of 0 to 900 K. Charge transfer investigations at the Fe/Nb-O sites have shown that on both the (010) and (111) surfaces the H atoms obtain electron density from Fe/Nb, whereas the electrons are transferred from the other dissociated H atom to the coordinated O atom.

Finally, we have simulated the migration of H ions and water formation at the Fe-O sites in the (010) surface and the O_{Fe} site of the (111) surface. The barriers for the

diffusion of H ions range from 0.44 to 0.54 eV on the three (010) surfaces, but is higher at 1.08 eV on the (111) surface. The lowest calculated barrier for the formation of surface-bound water is found for the O_{Fe} site of the (111) surface at 1.02 eV, which is close to that of other anode materials, *e.g.* Ni-YSZ and CeO₂.

Overall, our simulations suggest that the oxygen bridge sites both on the (010) or (111) surfaces display more chemical reactivity towards H₂ dissociation than the metaloxygen bridge sites. However, the diffusion of dissociated H ions from this site is less energetically favorable than from the Fe/Nb-O sites. We consider that this chapter, which has revealed the mechanisms of hydrogen dissociation and water formation at two major surfaces of disordered o-FeNbO₄, shows that this material has promising SOFCs anode characteristics and we trust that our study will provide guidance for future experimental work.

Chapter 5: Oxygen diffusion in the bulk

5.1 Abstract

In this chapter, we have first used site occupancy disorder (SOD) method [182] to confirm the configurations of the o-FeNbO₄ phase. We found that one ordered configuration of the stoichiometric o-FeNbO₄ structure dominates when analysing the probabilities of cation disorder in three supercells $(2 \times 2 \times 1, 2 \times 1 \times 2, \text{ and } 1 \times 2 \times 2)$. We then studied the bulk properties of this selected o-FeNbO₄ through DFT calculations, including the lattice parameters, the mechanical properties and the electronic structures, where no remarkable differences were observed compared to the monoclinic FeNbO₄ structure. Finally, because oxygen mobility is key to the successful application of o-FeNbO₄ as an electrode material, we have simulated the diffusion pathways of oxygen through both the stoichiometric and non-stoichiometric structures, where the results show that the existence of oxygen vacancies enhances diffusion and the distribution of the Fe and Nb inside the lattice affects the energy barriers and could therefore impact the oxygen diffusion.

5.2 Introduction

ABO₄-type oxides, *e.g.* FeWO₄, FeVO₄ or LaTaO₄, have shown significant promise as functional oxides in many applications, for example in super-capacitors and solar cell electrodes.[115, 116, 120, 123, 125] Generally, ABO4 materials can be classified into two types on the basis of the valence of element B, *i.e.* +5 or +6. ABO₄ oxides with B $= W^{6+}$ or Mo⁶⁺, have shown remarkable efficacy when used as super-capacitor and luminescence materials.[178, 179] For example, it has been reported that green photoluminescence emission of BaWO₄ polymer nanohybrids was observed when the tetrahedral WO₄ structure was changed to the octahedral WO₆ structure, and an intense blue photoluminescence emission could also occur in BaWO₄ powders due to the existence of defects around oxygen.[121, 178] Other ABO₄-type materials ($B = V^{5+}$, Nb⁵⁺ and Ta⁵⁺) mostly show catalytic behaviour to some degree, as well as potential as luminescence materials.[180, 181] For example, LaTaO₄ doped with Eu is an interesting material for energy applications, as it catalyses aqueous methanol to generate hydrogen, whereas the BiVO₄/FeVO₄ heterojunction also displays similar photocatalytic performance when used to generate hydrogen through the splitting of water molecules.[116, 180]

FeNbO₄, as a typical ABO₄ oxide, has shown good electrical and catalytic performance and thus has been developed for many years in applications such as gas sensing devices and solar energy conversion devices.[8, 13, 22] In recent years, both m- and o-FeNbO₄ materials have been explored for energy storage and conversion applications.[10, 30, 33] Interestingly, both m- and o-FeNbO₄ have shown potential as a replacement material for the Ni metal in the fuel electrode of SOC, although o-FeNbO₄ is more suitable in electrodes than m-FeNbO₄. It has been reported that, when m-FeNbO₄ is used as anode in SOFCs, there is a clear weight loss during its operation, [10] caused by the ordering within the m-FeNbO₄ system, where Fe³⁺ and Nb⁵⁺ layers are distributed alternately through the structure. Fe³⁺ is unstable, especially when exposed to a hydrogen atmosphere when it is easy for the Fe³⁺ to be reduced to the Fe²⁺, at the same time generating a water molecule, which causes the structure to collapse.[10] This does not occur in the disordered o-FeNbO₄ system and as such, o-FeNbO₄ may be the more promising material in energy conversion applications.

In the previous chapter, we have employed calculations based on the DFT to study the surface properties of the o-FeNbO₄ phase with random distributions of cations. However, this typical structure is not confirmed as the main configuration or one of the main configurations in a theoretical way. On the other hand, due to the disorder of the cations in the o-FeNbO₄ phase, it is more difficult to create a computational model to simulate its behaviours and properties, which is presumably the reason why few computational studies have been reported on the orthorhombic phase. In this chapter, we have employed the SOD code [182] to construct all the inequivalent cation configurations within the o-FeNbO₄ structure to identify the most stable structures. In addition, we have investigated the existence of oxygen vacancies, which according to experimental results and improve the electronic conductivity when introduced into the structure in small concentrations.[9, 183] There are few experimental reports on the diffusion of the oxygen within the material, and in this chapter, we have also employed

DFT calculations to investigate oxygen diffusion pathways, which are important in providing the oxygen required for the reaction with hydrogen, when the materials is used in catalytic electrodes.[10, 33, 34]

5.3 Computational method

5.3.1 Force field parameters

The GULP code [108-111] was employed to carry out calculations on a number of bulk properties. GULP is based on the Born model of ionic solids, which defines all atoms as charged spherical ions, and describes their interactions through short-range repulsive and Van der Waals forces and long-range Coulombic interactions.[112, 184, 185] The short-range interactions in this thesis are described through Buckingham potentials and we have applied the core-shell model for the polarizable oxygen ions, where the total charge of the oxygen anions is split between a massive core and a massless shell. Specifically, the IP parameters to describe the interactions between the Fe-O, Nb-O and O-O pairs are applicable to model both the monoclinic and orthorhombic FeNbO₄ phases. The Fe-O_{shell}, Nb-O_{shell} and O_{shell}-O_{shell} potentials used in this thesis are those reported by Woodley and Bush [186, 187] and are listed in Table 5.1. In addition, we have studied the effect of oxygen vacancies on the distribution of the cations in the orthorhombic phase, and to compensate the charges in the oxygen-vacant structures, we have assumed that the surplus electrons generated by the oxygen vacancy remain on the neighbouring iron ions, whose charge is reduced from Fe^{3+} to Fe^{2+} .

Daina	Buckingham potential parameters			
Pairs	A (eV)	ρ (Å)	$C \left(\mathrm{eV} \cdot \mathrm{\AA}^{6} \right)$	
Fe ³⁺ -O _S - ^{2.513}	3219.34	0.2641	0	
Fe ²⁺ -O _S - ^{2.513}	2763.94	0.2641	0	
Nb ⁵⁺ -O ₈ -2.513	3023.18	0.3	0	
Os ^{-2.513} -Os ^{-2.513}	25.41	0.6937	32.32	
Lon	Core-shell model parameters			
Ion	$Kcs(eV/Å^2)$	$q_{Oc}(\mathbf{e})$	$q_{Os}(e)$	
Oc ^{+0.513} -Os ^{-2.513}	20.53	+0.513	-2.513	

Table 5.1. Interatomic potential parameters used for the FeNbO4.

5.3.2 SOD method

We have employed the SOD code [182] to generate all of the Fe and Nb cation configurations within the orthorhombic FeNbO₄ structure. We have built $2 \times 2 \times 1$, 2×1 $\times 2$ and $1 \times 2 \times 2$ supercell models to obtain the energetically optimum mixed structures. All inequivalent configurations within the $2 \times 2 \times 1$, $2 \times 1 \times 2$ and $1 \times 2 \times 2$ models were transferred into the GULP code to calculate the free energies, which were then used in SOD to carry out the analysis of the probability distribution of the inequivalent configurations. We have also carried out the same process on non-stoichiometric $2 \times 2 \times$ 1 models, to determine the dominant phases when oxygen vacancies are present in the structure.

5.3.3 DFT simulations

In this chapter, all the DFT calculations were carried out using the Vienna Ab initio

Simulations Package, VASP (version 5.4.4) [126-129], where we obtained the bulk properties of the preferred o-FeNbO₄ model selected from the probabilities calculations above. The ion-electron interactions and the exchange-correlation interactions are described through the projector-augmented wave method (PAW) [96] and the generalized gradient approximation (GGA) [130] with the Perdew-Burke-Ernzerhof (PBE) density functional, respectively. Spin-polarization was employed in all calculations and we have treated the following as valence electrons: Fe $(3p^63d^74s^1)$, Nb $(4p^65s^14d^44s^2)$, O $(2s^22p^4)$. In addition, to improve the description of the electronic structures, we have used the on-site Coulombic interaction (DFT+U) [90] for the Fe 3d electrons with the U-J value of 4.3 eV.[131, 132] Following test calculations, the kinetic energy cut-off for the plane wave basis was set at 500 eV and the Henkelman algorithm was used to calculate the Bader charges.[133] In addition, 3×3×3 gamma centered Monkhorst Pack grids was used for the simulation of the $2 \times 2 \times 2$ bulk. We have considered the spin distribution of Fe atoms in the orthorhombic phase as a quasirandom one and this phase could be generated through the Alloy Theoretic Automated Toolkit (ATAT), which has employed in the special quasi-random structures (SQS) method.[169-172]

In the final part of the chapter, we have simulated the diffusion of oxygen through the o-FeNbO₄ lattice, where we have first placed an extra oxygen atom into an interstitial site inside the lattice and moved this atom by different methods. In order to obtain a good understanding of the diffusion pathways, we have employed the static lattice method, which has been used by Saadoune, Baykov and others, [188-190] to determine

the possible pathways. In this method, the diffusing atoms are fixed along the pathway, with the other atoms allowed to optimise fully, thereby avoiding the formation of stable structures which are not part of the diffusion pathways. Compared to the climbing image nudged elastic band (CI-NEB) method, which aims to find the saddle point in chemical reactions, the energy of transition states obtained through the static lattice method may be underestimated but it is a good description, and comparison, of different possible diffusion pathways.

5.4 GULP simulations

Elucidating the most probable cation configurations in the orthorhombic phase through the SOD and GULP codes needs suitable IP parameters. To this end, we have first employed the listed force field parameters in the GULP code to optimize the ordered monoclinic phase, and by evaluating whether the computational results are close to the experimental data, we could demonstrate the capability of the IP parameters to describe the interatomic interactions and next use them to simulate the orthorhombic phase.

The lattice parameters of the experimental m-FeNbO₄ structure are listed in Table 5.2. The four structures obtained from experiments have been plotted in Figure 5.1, and through comparing the structure of experiment 3 and 4, we found that exchanging the Fe position for Nb does not affect the octahedral arrangement and the structural properties. The difference between the structures of experiments 1-2 and 3-4 is that experiment 1 and 2 show a P 2/a symmetry, while the structures in experiment 3 and 4 have a symmetry of P 2/c, in which the parameters a and c are swapped compared to experiments 1 and 2. The computational results from the DFT calculations, discussed in detail in chapter 3 are generally more accurate than those obtained from GULP, where all lattice parameters except for the β angle exceed the original data (by 0.11 Å, 0.12 Å and 0.14 Å for a, b and c respectively). However, the error is within an acceptable margin and the force field parameters in Table 1 are accurate enough to employ in this thesis.



Figure 5.1. The 1×1×1 bulk structures obtained from experiments: (a) experiment 1; (b) experiment 2; (c) experiment 3; (d) experiment 4; red is oxygen, brown is Fe, and green is Nb.

	Experiment 1 ^[147]	Experiment 2 ^[2]	Experiment 3 ^[15]	Experiment 4 ^[5]	DFT	GULP
a	4.656	4.637	4.646	4.650	4.687	4.697
b	5.632	5.607	5.615	5.616	5.691	5.573
с	5.008	4.992	4.996	4.998	5.038	5.102
β	90.27	90.06	89.85	90.15	90.44	87.31
Fe (y)	0.6742	0.6687	0.6680	0.1713	0.1657	0.1528
Nb (y)	0.1807	0.1824	0.1811	0.6799	0.6813	0.6720
O1 (x)	0.9402	0.919	0.2270	0.2251	0.2311	0.2234
O1 (y)	0.138	0.116	0.1106	0.1187	0.1172	0.1021
O1 (z)	0.774	0.767	0.9227	0.9113	0.9161	0.9134
O2 (x)	0.425	0.418	0.2704	0.2981	0.2754	0.2684
O2 (y)	0.384	0.384	0.3812	0.3827	0.3853	0.3920
O2 (z)	0.725	0.738	0.4177	0.437	0.4228	0.4384

Table 5.2. Experimental and computational results for the monoclinic FeNbO₄ lattice cell. (The experimental data of 1, and 2 show a P 2/a symmetry, while the data of experiment 2 and 3 show a P 2/c symmetry.)

5.5 Dominant phase

In the SOD code, the number of inequivalent cation configurations of a $2 \times 2 \times 2$ supercell of the disordered o-FeNbO₄ materials would reach $C_{32}^{16} = \frac{32!}{16! \times 16!}$, which is an unrealistic number of configurations to compute. Thus, to still do a comprehensive study of the ordering in the structure, we have generated $2 \times 2 \times 1$, $2 \times 1 \times 2$, and $1 \times 2 \times 2$ supercells. From Table 5.3, we note that in each of these supercells the total number of inequivalent configurations is $C_{16}^{8} = \frac{16!}{8! \times 8!}$ is 12870, which reduces after consideration of the symmetry, to 482, 448, and 474 for the three supercells, respectively. The results of the calculations of the probability distributions are shown in Figure 5.2 from which it is clear that from 700 K to 1600 K, there is one inequivalent configuration (labelled No.91, No.81 and No.91) in each cell whose probability of occurrence exceeds 99.5%. If we expand each cell to a $2 \times 2 \times 2$ supercell, we see that all 3 cells obtained the same dominant and ordered phase as the most probably configuration. As such, from our calculations, it appears that the most stable phase is an ordered structure rather than the disordered materials observed experimentally.

	~			
Supercell	Cell numbers	Composition	Total configurations	Inequivalent configurations
	(111)		(N)	<i>(M)</i>
2×2×1	4	Fe ₈ Nb ₈ O ₃₂	12870	482
2×1×2	4	Fe ₈ Nb ₈ O ₃₂	12870	448
1×2×2	4	Fe ₈ Nb ₈ O ₃₂	12870	474

Table 5.3. Inequivalent configurations for the orthorhombic FeNbO₄.



Figure 5.2. The distributions of the probabilities in the $2 \times 2 \times 1$, $2 \times 1 \times 2$, and $1 \times 2 \times 2$ supercells and the related most stable configurations; red is oxygen anion, brown is the Fe cation and green is the Nb cation.

To further validate the IP parameters, we have optimised both the monoclinic and orthorhombic FeNbO₄ structures. The relaxed lattice energies and structural parameters are listed in Table 5.4. They show that the lattice energy of m-FeNbO₄ is lower than the o-FeNbO₄, which is consistent with experiment in that the m-FeNbO₄ should be more stable than o-FeNbO₄.

	<i>a</i> (Å)	b (Å)	<i>c</i> (Å)	β (°)	Lattice energy (eV)
m-FeNbO ₄	4.697	5.573	5.102	87.31	-481.795
o-FeNbO4	4.679	5.526	5.096	90.00	-481.687

Table 5.4. The lattice parameters and lattice energy of m-FeNbO4 and o-FeNbO4 from GULP simulations.

5.5.1 Bulk properties

Before optimising the structure, we have first confirmed the magnetic distribution inside the lattice, see Figure 5.3, according to research in chapter 3 where the orthorhombic structure shows antiferromagnetic behaviour with small areas of spin glass. We next carried out DFT calculations to obtain a range of properties of the selected o-FeNbO4, shown Table 5.5. As a comparison, we have added the same data for the m-FeNbO4 phase showing no remarkable difference in Bader charges or bond distances between the o-FeNbO4 and m-FeNbO4 structures. Interestingly, in the o-FeNbO4 structure, the magnetic moment of Fe could not maintain the same value as in the m-FeNbO4 structure, indicating that in a spin glass structure shown in Figure 5.3, the spin symmetry can be broken. In summary, both the results of the calculation of the probabilities and the electronic structure has demonstrated that the phase transition from the monoclinic to the orthorhombic structure does not impact the bulk properties.



Figure 5.3. The magnetic structure used in this chapter; red is oxygen, brown is Fe, and green is Nb.

	o-FeNbO4	m-FeNbO4
<i>q_{Fe}</i> (e)	+1.88	+1.89
<i>q_{Nb}</i> (e)	+2.72	+2.72
<i>q</i> ₀ (e)	-1.16/-1.31	-1.16/-1.30
<i>m_{sFe}</i> (µ _B)	(±)4.17~(±)4.25	4.27
<i>m_{sNb}</i> (µ _B)	0	0
<i>m_{sO}</i> (µ _B)	0	0
Fe-O distance(Å)	2.052	2.045
Nb-O distance(Å)	2.022	2.017

Table 5.5. Bader charge, magnetic moment and bond distance of the m/o-FeNbO4 lattice.

We have also calculated the mechanical properties of the ordered o-FeNbO4, including the elastic constants (C_{ij}), bulk modulus (B), shear modulus (G) and Young's modulus (E), again comparing with the m-FeNbO₄ material from chapter 3. We have employed VASP and the finite difference technique to obtain the values of the elastic constants C_{ij} , where the elastic tensor was obtained by performing finite distortions in the

direction of each Cartesian coordinate of the lattice and deriving C_{ij} through the stressstrain method as:

$$C_{ij} = \frac{1}{V} \frac{\partial^2 E}{\partial \varepsilon_i \partial \varepsilon_j} \quad (5-1)$$

where *E* is the total energy of the stressed cell, *V* is the equilibrium volume and ε is the component of the applied strain. Having calculated the values of C_{ij} , we obtain the values of *B*, *G*, and *E* through the following equations:

$$B = \frac{[c_{11} + c_{22} + c_{33} + 2(c_{12} + c_{13} + c_{23})]}{9} \quad (5 - 2)$$

$$G = \frac{[c_{11} + c_{22} + c_{33} + 3(c_{44} + c_{55} + c_{66}) - (c_{12} + c_{13} + c_{23})]}{15} \quad (5 - 3)$$

$$E = \frac{9BG}{3B + G} \quad (5 - 4)$$

In contrast to the monoclinic phase, there are 9 independent elastic constants (C_{11} , C_{22} , C_{33} , C_{44} , C_{55} , C_{66} , C_{12} , C_{13} , and C_{23}) for the orthorhombic structure, all listed in Table 5.6. We found that the C_{11} of m-FeNbO₄ is smaller than that of o-FeNbO₄, while the converse is true for the C_{33} , indicating that along its *a* direction the m-FeNbO₄ phase is softer, while along the *c* direction it is harder than the o-FeNbO₄ phase. Next, we employed equations (2-4) to calculate the values of the bulk modulus (*B*), the shear modulus (*G*) and the Young's modulus (*E*) and found that all moduli of the m-FeNbO₄ phase are a little larger than that of the o-FeNbO₄ phase, indicating the ability of the o-FeNbO₄ phase to resist compression and elastic shear strain and its tensile stiffness are not as good as that of the m-FeNbO₄ phase.

Elastic constant	m-FeNbO ₄	o-FeNbO ₄
C ₁₁ (GPa)	274.1	304.1
C ₂₂ (GPa)	269.8	271.4
C ₃₃ (GPa)	318.8	253.9
C44 (GPa)	74.5	27.6
C ₅₅ (GPa)	102.1	24.7
C66(GPa)	57.1	72.6
C ₁₂ (GPa)	144.1	141.3
C ₁₃ (GPa)	148.5	110.7
C ₂₃ (GPa)	119.7	140.7
C15 (GPa)	-6.8	-
C ₂₅ (GPa)	-11.7	-
C35 (GPa)	-22.9	-
C ₄₆ (GPa)	10.2	-
B (GPa)	187.5	179.4
G (GPa)	76.8	54.1
E (GPa)	202.7	147.5

Table 5.6. Elastic constants and the mechanical properties of the m/o-FeNbO4.

Finally, we have compared the electronic structure of the m- and o-FeNbO₄, whose DOS plot is shown in Figure 5.4. Generally, there is a very similar DOS distribution for the m/o-FeNbO₄ phases, except for a slight difference in the conduction band, where the integrated orbital in the α direction is split into two small parts in the DOS of o-FeNbO₄. Both phases show typical semiconductor characteristic with a band gap between the CBM and the VBM, where the CBM is mainly comprised of the Fe 3d orbitals. Furthermore, it is believed that in the m-FeNbO₄ phase, the electron conduction mainly occurs in the FeO₆ layers along its a direction while after mixing the Fe and Nb, it is likely that the electron could be conducted through the 3D net inside.



Figure 5.4. PDOS for the monoclinic FeNbO4 (a) and the orthorhombic FeNbO4 (b).

5.6 Oxygen vacancies.

5.6.1 Types of oxygen vacancies

In the ordered o-FeNbO₄ structure, there are two sites for the oxygen vacancy in the simulation cell, *i.e.* labelled V₀₁ which is surrounded by one FeO₆ and two NbO₆ octahedral, and labelled V₀₂ which is surrounded by two FeO₆ and one NbO₆ octahedral, shown in Figure 5.5. Before studying the diffusion of the oxygen in the nonstoichiometric phase, we have calculated the formation energies of the both vacancy types, also shown in Figure 5.5, according to the equation: $E_f = E_{defective} - E_{bulk} + \frac{1}{2}E_{O_2}$, where $E_{defective}$ and E_{bulk} are the total energies of the nonstoichiometric material and the stoichiometric bulk material, respectively, and E_{O_2} refers to the total energy of the oxygen molecule in the triplet ground state. Our simulations show that V₀₂ is the preferred oxygen vacancy site in the lattice due to its lower formation energy, although at 3.7 eV it is still a very high value, in agreement with experimental records which show that most oxygen vacancies are generated in the preparation process at temperatures of 1100 °C.[10, 183] We have therefore introduced the V₀₂ in the 2×2×2

supercells to investigate the oxygen diffusion pathways, where we noted that the formation energy of the oxygen vacancies does not change as the supercell size is increased in size, which indicates that the reduction is a localised process, also shown by the short-range lattice distortion around the vacancy sites.



Figure 5.5. Types of oxygen vacancies in the ordered o-FeNbO4; oxygen is red, Fe is brown, Nb is green and the red ball with black pattern represents the oxygen vacancy.

5.6.2 Inequivalent configurations

Since experimentally the orthorhombic phase is found to be disordered, we can also expect configurations with different Nb and Fe cation distributions to exist within the material. It has been reported that oxygen vacancies are found in the orthorhombic FeNbO₄ structure, which will increase cation mobility and the likelihood of cation disorder in the lattice.[9, 183, 191] We have demonstrated that the formation energy of oxygen vacancies depends on the oxygen site, and our earlier results suggest that if an oxygen were to be surrounded by three FeO₆ octahedra, the formation energy of the oxygen vacancy will be reduced even further. To test this hypothesis, we have created a $2\times2\times1$ supercell with this type of oxygen site and created the oxygen vacancy V₀₃, as shown in Figure 5.6. As suggested, the oxygen formation energy at 2.82 eV is indeed lower than that for the former two oxygen vacancy types (3.70 eV and 4.71 eV for V₀₂ and V₀₁ respectively). Next, we have investigated this oxygen-vacancy containing configuration with SOD and GULP to simulate the probabilities of its inequivalent configurations.



Figure 5.6. The third type of oxygen vacancy; oxygen is red, Fe is brown, Nb is green and the red ball with black pattern represents the oxygen vacancy.

The probabilities of the non-stoichiometric structures containing oxygen vacancies are plotted in Figure 5.7, where we observe four main structures from 700 K to 1600 K, in addition to the dominant structure, No.7069, which is shown in Figure 5.7b. These configurations are all different from the dominant stoichiometric phase, discussed

earlier, and our findings therefore suggest that when oxygen vacancies are present, cation disorder is more likely to occur, which could be the origin of the disordered materials found in experiment.



Figure 5.7. Distributions of the probabilities in the defect 2×2×1 supercell (a); the most stable No.7069 configuration (b) and the 2×2×2 supercell used in this chapter (c).

5.7 Oxygen Diffusion

5.7.1 Stoichiometric structure

Next, we have introduced an extra interstitial oxygen atom into the $2 \times 2 \times 2$ supercell, whose lattice is large enough that it does not affect imposed by the adjacent supercells. In the ordered stoichiometric o-FeNbO₄ structure, the lowest energy location for the insertion of an extra oxygen into the lattice is the interstitial site shown in Figure 5.8. The formation energy of the oxygen interstitial atom is relatively high at 2.2 eV and we would therefore not expect this defect to occur widely, but we have investigated this defect here for the sake of completeness.



Figure 5.8. Stable interstitial site of the extra oxygen in the 2×2×2 supercell.

Once, an interstitial oxygen atom has been inserted in the supercell, this oxygen atom could move to the adjacent interstitial site through pathways in the 3D networks. We have considered a number of plausible diffusion pathways, along the [100], [010], and [001] directions, see Figure 5.9-5.11. Along the [001] direction, the diffusion starts from the interstitial site, and then moves towards to the gap site, where an energy barrier (up to 3.18 eV) needs to be overcome to diffuse to the adjacent interstitial site. This behaviour is not unique to the [001] direction and other pathways can be seen in the Figure 5.10 and 5.11.



Figure 5.9. Diffusion pathway of the interstitial oxygen atom along the [001] direction in the ordered stoichiometric structure (a), and the variation of the total energy (b); red is oxygen, brown is Fe, green is Nb and the yellow ball in (b) is the interstitial oxygen atom.



Figure 5.10. Diffusion pathway of the interstitial oxygen atom along the [100] direction (a) and the [010] direction (b) in the NbO₆ network of the ordered stoichiometric structure and their related variation of the total energy (c-d); red is oxygen, brown is Fe, and green is Nb and the yellow ball in (c,d) is the interstitial oxygen atom.



Figure 5. 11. Diffusion pathway of the interstitial oxygen atom along the [100] direction (a) and the [010] direction (b) in the FeO₆ network of the ordered stoichiometric structure and their related variation of the total energy (c-d); red is oxygen, brown is Fe, and green is Nb and the yellow ball in (c,d) is the interstitial oxygen atom.

In addition to the direct diffusion pathway, we have also studied the interstitialcy mechanism along the [001] direction, which is the dominant diffusion pathway in many metal oxides.[192, 193] The result is plotted in Figure 5.12, showing an initial energy barrier of 3.89 eV, *i.e.* considerably larger than in the direct diffusion pathway. This therefore suggests that in FeNbO₄ materials the direct diffusion pathway should dominate, owing to the energetic cost of moving a lattice oxygen to the interstitial site compared to it moving through a gap site.



Figure 5.12. Diffusion pathway of the interstitial mechanism along the [001] direction in the ordered stoichiometric structure (a), and the variation of the total energy (b); red is oxygen, brown is Fe, green is Nb and the yellow ball in (b) is the interstitial oxygen atom.

5.7.2 Non-stoichiometric structure

Usually, the oxygen atom in the defect oxide materials prefer to diffuse through a hopping mechanism, similar to the process reported in BaFeO₃, SrCoO₃, and CeO₂ materials.[194-197] Figure 5.13 shows two possible pathways for this type of diffusion, where in Figure 5.13a, the oxygen atom hopping occurs along the [001] direction with the nearest neighbouring oxygen hopping into the original and newly generated vacancy sites. The energy barriers are shown in Figure 5.11b, where the vacancy sites 2 and 4 (type V₀₁) are less stable than other three (1, 3 and 5 which are type V₀₂ vacancies). Thus, from step 1 to 2, there is an energy barrier of ~1.04 eV, similar to the barrier from step 2 to 33 (~1.03 eV). Finally, when the vacancy is transferred to site 5 (V₀₂) from 4 (V₀₁), the structure tends to be stable again.

Along the [110] direction (Figure 5.13c), which can be seen as the combination diffusion way of [010] and [100], all the energy barriers have similar values (\sim 0.2 eV), since all vacancies along this pathway are type V₀₂ vacancies. Therefore, although the

oxygen could diffuse through the vacancy sites in the [100] way, the [110] pathway is energetically favourable. As expected, the presence of oxygen vacancies benefits oxygen diffusion through the lattice. In addition, we have noticed that for the oxygen atom, diffusing in the [110] direction is much easier than the [001] direction, since in the ordered structure all the vacancies along the [110] belong to the V_{02} type.



Figure 5.13. Diffusion pathways of the oxygen atom along the [001] direction (a) and the [110] direction (c) in the ordered non-stoichiometric structures with an oxygen vacancy and their corresponding energy barriers (b and d); red is oxygen, brown is Fe, green is Nb and the red ball with black pattern represents the oxygen vacancy.

In order to gain insight into the impact of the cation distribution on the oxygen diffusion, we have employed the $2\times2\times2$ supercell in Figure 5.7c, with different cation distributions along the diffusion pathways. In order to make the calculations tractable, we have selected pathways where the oxygen diffuses through a vacancy hopping mechanism. The same two pathways as identified in the ordered structure are plotted in Figure 5.14. Along the [001] direction, there is the distribution of vacancy types: V₀₃(step1) - V₀₁(step2) - V₀₂(step3) - V₀₂(step4) - V₀₃(step5), in contrast to the ordered structured where V_{01} and V_{02} alternate. From step 1 to step 2, the energy barrier to be surmounted is 2.09 eV to create V_{01} , where the total energy of the system is almost at its highest, before the vacancy hops to the more stable V₀₂ type, only having to overcome a very small further barrier of 0.15 eV. Next on the pathway, another V_{02} is created, for which an energy barrier of 0.59 eV has to be overcome, followed by a similar barrier of 0.62 eV to finally form another V₀₃. Similar results are found in the [110] direction, where in the first two steps, the vacancy moves from V_{03} to V_{01} with a barrier of 2.10 eV, but releasing 0.66 eV to form a V₀₁ site. When we compare these results with the diffusion in the ordered structure in Figure 5.13, we note that in the disordered structure the initial energy barrier for the oxygen to move into the V₀₃ site at about 2.10 eV is much higher than in the ordered structure, owing to the stability of the V₀₃ vacancy, and oxygen diffusion through the disordered structure will therefore be slower.



Figure 5.14. Diffusion pathways of the oxygen atom along the [001] direction (a) and the [110] direction (c) in the disordered non-stoichiometric structures with an oxygen vacancy and their corresponding energy barriers (b and d); red is oxygen, brown is Fe, green is Nb and the red ball with black pattern represents the oxygen vacancy.

5.8 Chapter conclusion

In this chapter, we further created the $2 \times 2 \times 1$, $1 \times 2 \times 2$ and $2 \times 1 \times 2$ supercells for the o-FeNbO₄ material to confirm the dominant cation configuration(s) within the o-FeNbO₄ structures, and we have studied the related bulk properties of the dominant o-FeNbO₄ phase obtained from the DFT simulations. For the stoichiometric material, the results all confirmed a single dominant, ordered configuration with a probability of occurrence that exceeds 99.5%, which was selected for more in-depth study. The bulk properties of this selected o-FeNbO₄ phase were obtained through DFT calculations, which showed that there is no remarkable difference from the m-FeNbO₄ phase, which was studied in chapter 3. We have also investigated the probabilities of cation disorder in the non-stoichiometric material containing an oxygen vacancy, where we identified a number of potential cation configurations. We therefore suggest that oxygen vacancies, which are present in experimental materials, may encourage the cation disorder in the orthorhombic FeNbO₄ phase observed experimentally.

We have simulated oxygen diffusion pathways in the ordered stoichiometric material and in the non-stoichiometric ordered and disordered structures. In the stoichiometric material, the diffusion of an interstitial oxygen atom could occur only by surmounting an energy barrier of around 3 eV, whereas in the non-stoichiometric ordered structure, it is much easier for the oxygen to diffuse in a vacancy hopping mechanism along the [110] direction (energy barrier up to ~ 0.24 eV) than along the [001] direction (up to \sim 1.04 eV), since in the [110] direction all the diffusion sites belong to the V₀₂ vacancy type, while in the [001] direction, some sites are of the energetically less favourable V₀₁ type. In addition, we found that the distribution of the cations in the structure could impact the energy barriers along the pathways. In particular, during the vacancy hopping mechanism, vacancies are more stable in sites which are coordinated by fewer Nb-O bonds and more Fe-O bonds. When a disordered structure contains the lowenergy V_{03} vacancy sites, the initial energy barrier for vacancy hopping is ~2.10 eV, and oxygen diffusion through non-stoichiometric disordered structures should therefore be slower.

We consider that this chapter has contributed detailed atomic-level insight into the FeNbO₄ material, where our results suggest that intrinsic oxygen vacancies promote

oxygen diffusion through the vacancy hopping mechanism, but cation disorder may slow oxygen diffusion by allowing more stable vacancy sites to be formed. These are therefore two parameters that could be the focus in experimental syntheses to improve the efficacy of FeNbO₄ as a cathode material in solid oxide fuel cells.
Chapter 6: Effect of Dopants on the o-FeNbO₄

6.1 Abstract

The low electronic conductivity of the material specifically in the pure structure without defects or dopants limits its practical applications as the fuel electrode of SOC. In this chapter, we have employed DFT + *U* calculations to explore the bulk and electronic properties of two types of doped structures, $Fe_{0.9375}A_{0.0625}NbO_4$ and $FeNb_{0.9375}B_{0.0625}O_4$ (*A*,*B* = Ti, V, Cr, Mn, Co, Ni) and the oxygen-deficient structures $Fe_{0.9375}A_{0.0625}Nb_1O_{3.9375}$ and $FeNb_{0.9375}B_{0.0625}O_{3.9375}$, where the dopant is positioned in the first nearest neighbour (1st NN) site to the oxygen vacancy. Our DFT simulations have revealed that doping in the Fe sites is energetically favourable compared to doping in the Nb site, resulting in significant volume expansion. The doping process generally requires less energy when the O-vacancy is surrounded by one Fe and two Nb ions. The simulated PDOS of the oxygen-deficient structures indicates that doping in the Fe site, particularly with Ti and V, considerably narrows the band gap to ~0.5 eV, whereas doping with Co at the Nb sites generates acceptor levels close to 0 eV. Both doping schemes therefore enhance electron conduction during SOFCs operation.

6.2 Introduction

FeNbO₄ gained initial recognition as a hydrogen sensor in the early 21th century.[6, 8] In recent years, research on this material has diversified into various applications, including as dielectric ceramic materials, [24, 25] anode materials for lithium-ion batteries and catalytic electrodes.[10, 30, 31] Notably, exploration of the orthorhombic phase with a disordered cation distribution as an alternative material for anodes of SOFCs has provided new insights into the stability and catalytic performance of such Fe-based anode materials.[10, 34] Previous experimental studies have shown that the orthorhombic FeNbO₄ anode material exhibits robust resistance to sulphur poisoning and a good electric conductivity of ~0.7 S·cm⁻¹, which is over ten times larger than the commonly used La_{0.75}Sr_{0.25}Cr_{0.5}Mn0.₅O₃ anode.[198, 199]

Despite these promising attributes, our previous chapters and other experimental results [146, 200], have revealed that the band gap of the pure orthorhombic FeNbO₄ material is around 2.2 eV, which limits its electronic conductivity. To address this limitation, Ti⁴⁺ dopants have been introduced to substitute both Fe³⁺ and Nb⁵⁺ ions.[10] However, the full impact of these dopants on the structural and electronic properties remains poorly understood. In this chapter, we have substitutionally doped the Fe and Nb sites of both the stoichiometric and O-deficient o-FeNbO₄ structures by the first-row transition metal atoms Ti, V, Cr, Mn, Co and Ni. The stoichiometric and O-deficient o-FeNbO₄ structures are the same as those in the last chapter. We have employed calculations based on the DFT method to evaluate the feasibility of incorporating these dopants into the material, fully characterising their effect on the structural and electronic properties,

which is crucial in guiding future experimental work.

6.3 Computational method

6.3.1 DFT calculations

We have employed the Vienna Ab initio Simulation Package, VASP (version 5.4.4), [126-129] to carry out the DFT calculations of the FeNbO₄ models. The frozen ionelectron interactions were modelled using the projector-augmented wave method (PAW).[96] We have treated the following as valence electrons: $Fe(3p^63d^74s^1)$, Nb($4p^{6}5s^{1}4d^{4}4s^{2}$), O($2s^{2}2p^{6}$), Ti($3s^{2}3p^{6}3d^{2}4s^{2}$), V($3s^{2}3p^{6}3d^{4}4s^{1}$), Cr($3p^{6}3d^{5}4s^{1}$), $Mn(3p^63d^54s^2)$, $Co(3p^63d^74s^2)$ and Ni $(3p^63d^84s^2)$. We have used the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) [130] exchangecorrelation functional for all the spin-polarized calculations. Partial occupancies were taken into account using the tetrahedron method with Blöchl corrections. The magnetic structure considered in this chapter is illustrated in Figure 6.1 and the rationale for this choice is discussed in previous chapter. To enhance the description of the electronic structures, we have incorporated the on-site Coulombic interaction (DFT+U) [90] for Fe-3d, Ti-3d, V-3d, Cr-3d, Mn-3d, Co-3d and Ni-3d electrons with the Ueff values set at 4.3 eV, 3.5 eV, 3.5 eV, 3.5 eV, 4.0 eV, 4.5 eV and 5.0 eV, respectively. After test calculations, the kinetic energy cut-off for the plane wave basis set was set at 500 eV, and the Henkelman algorithm was employed to calculate the Bader charges.[133] A $3 \times 3 \times 3$ gamma-centered Monkhorst-Pack grid was used to simulate the bulk models and structural optimisations were carried out using the conjugate gradient method, terminating when forces were converged within 0.01 eV/Å. The electronic energy was considered optimised when it exhibited a change of less than 10^{-5} eV between two consecutive self-consistent loops.

6.3.2 Doping energy

We represent the doping process in both stoichiometric ($Fe_{16}Nb_{16}O_{64}$) and O-deficient $Fe_{16}Nb_{16}O_{63}$ using the Kröger-Vink notation equations 6-1-6-4. This notation is a set of conventions employed to describe the positions of point defects and charges within the crystal. We have designated A/B_xO_y as the metal oxide phases TiO₂, V₂O₅, Cr₂O₃, MnO₂, Co₃O₄ and NiO in their most stable structures, *i.e.* with the space groups P4₂/mnm, P2₁/m, R3c, P4₂/mnm, Fd3m and Fm3m, respectively. The lattice parameters for these structures are listed in Table 6.1.

Oxides	Space group	a (Å)	b (Å)	<i>c</i> (Å)	α (°)	β (°)	γ (°)
TiO ₂	P 42/mnm	4.594	4.594	2.959	90	90	90
V_2O_5	P1 21/m	7.114	3.572	6.285	90	90.07	90
Cr ₂ O ₃	R-3cH	4.785	4.785	13.162	90	90	120
MnO ₂	P 42/mnm	4.400	4.400	2.870	90	90	90
C0 ₃ O ₄	Fd-3mZ	8.082	8.082	8.082	90	90	90
NiO	Fm-3m	4.180	4.180	4.180	90	90	90

Table 6.1. Lattice parameters oxides used in this chapter.

Note that the coefficient of O_2 is negative when the structure is doped with NiO at the Fe site and NiO, Cr_2O_3 , MnO_2 and Co_3O_4 at the Nb site, indicating that this gas molecule is a reactant and not a product.

$$\frac{1}{x}A_{x}O_{y}(s) + Fe_{16}Nb_{16}O_{64}(s) \leftrightarrow Fe_{15}ANb_{16}O_{64}(s) + \frac{1}{2}Fe_{2}O_{3}(s) + \frac{2y-3x}{4x}O_{2} \quad (6-1)$$

$$\frac{1}{x}B_{x}O_{y}(s) + Fe_{16}Nb_{16}O_{64}(s) \leftrightarrow Fe_{16}Nb_{15}BO_{64}(s) + \frac{1}{2}Nb_{2}O_{5}(s) + \frac{2y-5x}{4x}O_{2} \quad (6-2)$$

$$\frac{1}{x}A_{x}O_{y}(s) + Fe_{16}Nb_{16}O_{63}(s) \leftrightarrow Fe_{15}ANb_{16}O_{63}(s) + \frac{1}{2}Fe_{2}O_{3}(s) + \frac{2y-3x}{4x}O_{2} \quad (6-3)$$

$$\frac{1}{x}B_{x}O_{y}(s) + Fe_{16}Nb_{16}O_{63}(s) \leftrightarrow Fe_{16}Nb_{15}BO_{63}(s) + \frac{1}{2}Nb_{2}O_{5}(s) + \frac{2y-5x}{4x}O_{2} \quad (6-4)$$

The doping energy (E_{doping}) is calculated as the sum of the energies of the products minus the sum of the energies of the reactants multiplied by their respective coefficients in the chemical equations 1 to 4.

6.4 Stoichiometric o-FeNbO4

First, we have investigated the impact of the transition metal dopants on the structural and electronic properties of FeNbO₄. We have employed both the ordered stoichiometric structure and the O-deficient structure in the configuration with the largest probability, as identified in last chapter, see Figure 6.1. It is crucial to note that the lowest energy stoichiometric FeNbO₄ structure exhibits an ordered distribution of cations, characterised by a single ionic arrangement, whereas the O-deficient structure is disordered and is represented by multiple configurations, which are demonstrated in the previous chapter.



Figure 6.1. (a) Stoichiometric and (b) O-deficient structures showing the magnetic configurations employed in this study. O is shown in red, Fe in brown and Nb in green.

In this chapter, we have continued to use the $2 \times 2 \times 2$ supercell of FeNbO₄, which size is sufficient to capture the random cation distribution and simulate the bulk properties of the doped Fe_{0.9375}A_{0.0625}NbO₄/FeNb_{0.9375}B_{0.0625}O₄ oxygen-deficient and $Fe_{0.9375}A_{0.0625}NbO_{3.9375}/FeNb_{0.9375}B_{0.0625}O_{3.9375}$ configurations. Specifically, when introducing one dopant atom into the Fe or Nb sites of the 2×2×2 supercell, the stoichiometry was reduced from 1 to 0.9375, where the subscript 3.9375 means that one oxygen vacancy was generated in the simulation cell. After testing various magnetic structures in Figure 6.2, we determined that the stoichiometric material adopts an antiferromagnetic configuration, where the alternating Fe layers along the c axis have opposite spin directions, see Figures 6.1 (a). In contrast, the most stable configuration for the O-deficient structure involves spins of the Fe in the layer containing only these cations aligning in the opposite direction to the spins in the mixed layers, which are parallel, as shown in Figure 6.2.



Figure 6.2. The three magnetic structures examined in this study along with the corresponding energies per formula; O is red, Fe is brown and Nb is green.

6.4.1 Bulk properties

The stoichiometric FeNbO₄, modelled as a $2 \times 2 \times 2$ supercell and belonging to the space group Pbcn, comprises 16 Fe, 16 Nb and 64 O atoms (Fe₁₆Nb₁₆O₆₄). Given that all Fe and Nb ions reside in the same Wyckoff 4c site, our approach involves selectively substituting one Fe and one Nb site at a time for the doping process, see Figure 6.3. Initially, we have scrutinised the effect of dopants in the Fe site on the lattice parameters, which are summarised in Table 6.2. Across all structures with dopants in the Fe site, we observed a tendency for lattice elongation along the *a* axis, while the Co and Ni dopants resulted in a reduction of the b and c lengths of the cell. Our computations indicate that post-doping, the α and γ angles of all structures have remained at 90°, while the β angle deviated by no more than 0.08° from the ideal right angle of the parent material, whereas the Mn- and Ti-doped systems exhibited an overestimation of the β angle. The y coordinate experienced a slight overestimation in comparison to the ideal 4c Wyckoff position value of 0.1786. This implies a minor shift of the dopants along the b direction with minimal impact on the lattice shape. Additionally, we have computed the volume $V = a \times b \times c \times \sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2\cos \alpha \cos \beta \cos \gamma}$ as and the

volume change as $\frac{\Delta V}{V} = \frac{V_{doped} - V_{undoped}}{V_{undoped}}$. Our findings indicate that structures doped with Co or Ni underwent a marginal compression along the *b* and *c* directions. In contrast, doping with Ti, V, Cr and Mn led to a volume expansion with the Ti-doped structure exhibiting the most significant increase at 0.368%. Notably, the observed effects of first row transition metal dopants on volume align closely with previous research, where the introduction of Ti and Cr on the Mn site of NaMnO₂ resulted in volume stretching, while Co and Ni, possessing larger atomic numbers than Mn, led to volume compression.[201]



Figure 6.3. Optimised structures of FeNbO₄ with Co, Cr, Mn, Ni, Ti and V dopants on the (a) Fe site and (b) Nb site; O is red, Fe is brown, Nb is green and dopants are dark blue.

Table 6.2. Lattice parameters, y coordinate of dopants and volume of the FeNbO₄ structure with dopants incorporated at the Fe site.

<i>A</i> , <i>B</i>	a (Å)	b (Å)	<i>c</i> (Å)	α (°)	β (°)	γ (°)	у	V (Å ³)	$\Delta V/V (\%)$
Stoichiometric	9.407	11.380	10.046	90	90	90	0.1786	1075.627	-
Ti	9.421	11.388	10.062	90	90.01	90	0.1809	1079.584	0.368
V	9.414	11.387	10.056	90	89.94	90	0.1828	1077.887	0.210
Cr	9.411	11.382	10.048	90	89.97	90	0.1858	1076.271	0.060
Mn	9.417	11.394	10.039	90	90.15	90	0.1823	1077.232	0.149
Со	9.412	11.376	10.045	90	89.97	90	0.1806	1075.459	-0.015
Ni	9.408	11.375	10.045	90	89.92	90	0.1833	1075.045	-0.054

Table 6.3 shows that structures containing dopants at the Nb sites are compressed in all

three crystallographic directions, barring the expanded *c* parameter observed in the Tidoped structure. Our simulations show that the lattice structure tends to adopt a triclinic form, with all lattice angles deviating from 90° by no more than 0.18°. Notably, the α and *y* angles of the V-doped structure maintain the ideal right angles. Furthermore, the *y* coordinates of dopants at the Nb sites tend to be underestimated compared to the value in the parent material of 0.1786, except for the structure containing V. Our calculated volumes for the doped structures are consistently smaller than those of pure FeNbO4, with the Mn-doped material, exhibiting the most significant reduction of 0.556%. In general, our findings indicate that doping the Nb site induces a greater degree of symmetry breaking compared to doping the Fe site, resulting in the formation of triclinic structures. Crucially, our calculations reveal a volume decrease solely for FeNb0.9375*B*0.0625O4, with respect to FeNbO4, underscoring the prominent role of Nb site doping in reducing the overall volume of the material.

<i>A</i> , <i>B</i>	<i>a</i> (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	У	V (Å ³)	$\Delta V/V(\%)$
Stoichiometric	9.407	11.380	10.046	90	90	90	0.1786	1075.627	-
Ti	9.402	11.374	10.052	89.97	89.82	90.06	0.1764	1075.036	-0.055
V	9.390	11.378	10.031	90	89.92	90	0.1817	1071.851	-0.351
Cr	9.387	11.380	10.026	89.97	89.90	90.05	0.1750	1071.000	-0.430
Mn	9.383	11.355	10.039	90.04	89.82	90.02	0.1630	1069.650	-0.556
Со	9.391	11.369	10.034	89.91	89.95	89.93	0.1684	1071.420	-0.391
Ni	9.385	11.368	10.038	89.85	89.83	90.16	0.1525	1071.011	-0.429

Table 6.3. Lattice parameters, *y* coordinate of dopants and volume of the FeNbO₄ structure with dopants incorporated at the Nb site.

The Bader charges for both $Fe_{0.9375}A_{0.0625}NbO_4$ and $FeNb_{0.9375}B_{0.0625}O_4$ structures are presented in Table 6.4. We observe a consistent decrease in the Bader charges of first

row transition metal dopants at the Fe site, following the order $q_{TI} > q_V > q_{Cr} \approx q_{Mn} > q_{Co} > q_{Ni}$, which is consistent with their respective positions in the periodic table. Our calculations indicate that the Bader charges of O, Fe, and Nb remain constant with respect to the stoichiometric structure, except for Ti- and V-doped structures, where the Bader charge of oxygen exhibits a marginal increase. We noted a similar trend in the Bader charges of dopants between FeNb_{0.9375}B_{0.0625}O₄ and Fe_{0.9375}A_{0.0625}NbO₄. Additionally, the Bader charge of oxygen experiences a negligible reduction in structures containing Cr, Mn, Co and Ni. Our DFT calculations indicate that Bader charges of dopants tend to be larger at the Nb site than at the Fe site. This observation suggests a greater likelihood for the Nb site to form stronger ionic interactions with the crystal than its Fe counterpart.

		Fe	e site		Nb site				
A, B	<i>q</i> _A (e)	<i>q</i> ₀ (e)	<i>q_{Fe}</i> (e)	<i>q_{Nb}</i> (e)	<i>q</i> _B (e)	<i>q</i> ₀ (e)	<i>q_{Fe}</i> (e)	<i>q_{Nb}</i> (e)	
Stoichiometric	-	-1.14	+1.86	+2.72	-	-1.14	+1.86	+2.72	
Ti	+2.11	-1.15	+1.86	+2.72	+2.44	-1.14	+1.86	+2.72	
V	+1.97	-1.15	+1.86	+2.72	+2.31	-1.14	+1.86	+2.72	
Cr	+1.84	-1.14	+1.86	+2.72	+2.06	-1.13	+1.86	+2.72	
Mn	+1.81	-1.14	+1.86	+2.72	+1.92	-1.13	+1.86	+2.72	
Со	+1.67	-1.14	+1.86	+2.72	+1.63	-1.13	+1.86	+2.72	
Ni	+1.52	-1.14	+1.86	+2.72	+1.41	-1.12	+1.86	+2.72	

Table 6.4. Atomic Bader charges (q) in the doped FeNbO₄structure.

Next, we have calculated the magnetic moments of the cations in the stoichiometric and doped materials, shown in Table 6.5. The magnetic moment of Fe is underestimated at $4.27 u_B$, a value in close agreement with previous findings.[200] The magnetic moments of the dopants thend to increase with atomic number from Ti to Mn, followed by a

decrease from Mn to Ni. Moreover, the valence states of cations in the stoichiometric and doped materials can be deduced from their magnetic moments. In the $Fe_{0.9375}A_{0.0625}NbO_4$ structure, we have approximated the magnetic moments of dopants to the nearest integer, resulting in $m_s(Fe) = 5 \mu_B$, $m_s(Nb) = 0 \mu_B$, $m_s(Ti) = 1 \mu_B$, $m_s(V) =$ 2 μ_B , $m_s(Cr) = 3 \mu_B$, $m_s(Mn) = 4 \mu_B$, $m_s(Co) = 3 \mu_B$, and $m_s(Ni) = 2 \mu_B$. All cations, including dopants, are in octahedral coordination, splitting the 3d orbital into three degenerate t_{2g} orbitals $(d_{xy}, d_{xz} \text{ and } d_{yz})$ and two also degenerate eg orbitals $(d_{x^2-y^2}, d_{yz})$ and d_{z^2}). Specific magnetic arrangements for Fe-substituted structures reveal that Cr, Mn, Ti and V are in the +3 valence state, while Co and Ni are in the +2 oxidation state. Additionally, we have calculated the magnetic moment of dopants at the Nb site, all displaying a relatively low-spin state. The values considered to evaluate the valence state are as follows: $m_s(Ti) = 0 \mu_B$, $m_s(V) = 0 \mu_B$, $m_s(Cr) = 2 \mu_B$, $m_s(Mn) = 3\mu_B$, $m_s(Co)$ = 3 μ_B , and $m_s(Ni) = 1 \mu_B$. Our calculations show that only the valence state of Ni was underestimated at +1, which is a state uncommon for Ni. Comparing valence states in both the Fe and Nb sites, we observe that, except for the Co dopant, the magnetic moments of the other dopants are lower than the corresponding values at the Fe site. This correlates with an increase in valence states from +2 to +4 for Cr, Mn and Ti and from +3 to +5 for V. Furthermore, the valence states of Co and Ni in the $Fe_{0.9375}A_{0.0625}NbO_4$ structure is smaller than that of the substituted Fe^{3+} , suggesting that oxygen donated electrons to these two dopants, a trend which is also evident in Ti-, Cr-, Mn-, Co- and Ni-doped FeNb_{0.9375}B_{0.0625}O₄ structures.

F	Fe site		Nb site			
А, В	<i>m</i> s (µB)	VS	<i>m</i> _s (µ _B)	VS		
Stoichiometric	4.27-(Fe)	+3	0-(Nb)	+5		
Ti	0.80	+3	0	+4		
V	1.86	+3	0	+5		
Cr	2.91	+3	1.60	+4		
Mn	3.85	+3	3.03	+4		
Co	3.13	+2	2.59	+2		
Ni	2.05	+2	1.09	+1		

Table 6.5. Atomic magnetic moments (m_s) , and valence states (VS) of the doped FeNbO₄ structure.

The Shannon's effective radius for each dopant and their doping energies into FeNbO₄ are detailed in Table 6.6. Shannon's reported effective ionic radii [202] are contingent on the valence and spin states of the transition metal atom. When Co and Mn occupy the Fe site, two possible magnetic structures emerge: high-spin states with magnetic moments of 3 and 4 μ_B , respectively, or low-spin states, with magnetic moments of 1 and 2 µ_B, respectively, see Figure 6.4. Our calculations indicate that the magnetic moments of Co and Mn align closely with high-spin states, measuring 3 and 4 $\mu_{\rm B}$. respectively. In contrast, Ti, V, Cr and Ni exhibit only one magnetic configuration, as illustrated in Figure 6.4. Our calculations show that only Ti³⁺ possesses a larger radius (0.670 Å) than Fe^{3+} in the parent structure, whereas Mn^{3+} and Fe^{3+} have very similar sizes, which is expected from their relative positions in the periodic table, see Table 6.5. Furthermore, the radii of V^{3+} and Cr^{3+} atoms, calculated as 0.640 and 0.615 Å, respectively, are smaller than Fe³⁺. In contrast, Co²⁺ and Ni²⁺ feature larger radii than Fe³⁺, attributed to their distinct oxidation states. The calculated doping energies imply that inserting V^{3+} , Cr^{3+} or Mn^{3+} is generally more facile than replacing Fe with Co^{2+} , Ni²⁺ or Ti³⁺. Additionally, we found that dopant size correlates with doping energy, evidenced by the sequence $R_{\text{Co}} > R_{\text{Ni}} > R_{\text{Ti}} > R_{\text{Mn}} > R_{\text{V}} > R_{\text{Cr}}$ and the order of doping energy as $E_{\text{Ti}} > E_{\text{Co}} > E_{\text{Ni}} > E_{\text{V}} > E_{\text{Mn}} > E_{\text{Cr}}$. This suggests that dopants with smaller radii find it easier to replace Fe than those with large radii with the exception of Ti and V.



Figure 6.4. Octahedral field splitting for the 3d orbitals and corresponding electron occupation of dopants on the Fe site of FeNbO₄.

For the dopants at the Nb site, we employed Shannon's effective radii for Co^{2+} in the high-spin state, while other dopants exhibit only one electronic configuration for their oxidation state, see Figure 6.5. Table 6.6 shows that only Ti^{4+} , V^{5+} , Cr^{4+} , and Mn^{6+} and have smaller radii than Nb⁵⁺. It worth noting that we have considered the Ni dopant to display the +1 state, rather than the +3 state. One reason is that Ni has a higher electronic negativity than Co which displays the +2 state, and another is that the Ni¹⁺ should have

relatively larger radii, which corresponds well with the volume change. Our calculated doping energies indicate that incorporating V at the Nb site is the easiest process, while the inclusion of other cations, particularly Cr or Co, is less favourable. However, no discernible relationship is apparent between the radii of first-row transition metal atoms and their doping energies, indicating a substantial disparity with the size of Nb, a second-row transition metal atom. In general, the radii of dopants on the smaller Fe site are larger than on the larger Nb site, except for Co and Ni, which explains the larger doping energies on the latter site.



Figure 6.5. Octahedral field splitting for the 3d orbitals and corresponding electron occupation of dopants on the Nb site of FeNbO4.

	Fe site		Nb site				
A, B	<i>R</i> (Å)	E_d (eV)	<i>R</i> (Å)	E_d (eV)			
Stoichiometric	0.645	-	0.690	-			
Ti	0.670	1.67	0.605	2.30			
V	0.640	0.85	0.540	1.34			
Cr	0.615	0.12	0.550	7.22			
Mn	0.645	0.26	0.530	3.60			
Со	0.745	1.26	0.745	9.17			
Ni	0.690	0.92	-	3.70			

Table 6.6. Shannon effective ionic radii (R) and doping energy (E_d) for the doped FeNbO₄ structure.

6.4.1 PDOS

We have plotted the PDOS for both stoichiometric and doped FeNbO₄ to elucidate the impact of the first-row transition metal dopants on the electronic structures. The electronic states of the 1st nearest neighbour (NN) ions to the dopant site were selected for display, owing to the symmetry of the stoichiometric structure, see Figure 6.6.



Figure 6.6. Selected intrinsic ions, marked with a star, for the projected density of states (PDOS) in the doped (a) Fe0.9375A0.0625NbO4 and (b) FeNb0.9375B0.0625O4 structures; O is red, Fe is brown and Nb is green.

Figure 6.7 illustrates that stoichiometric FeNbO₄ behaves as a semiconductor with a

PDOS band gap of 2.2 eV. The t_{2g} valence level and e_g conduction state of Fe emerge at approximately -7 and 2 eV, respectively, aligning with the 3+ oxidation state for this cation in the $Fe_{t2g\uparrow\uparrow\uparrow}^{eg\uparrow\uparrow}$ electronic distribution. Meanwhile, the t_{2g} and e_g orbitals of Nb are exclusively observed in the conduction band above 3 eV, given that this cation is fully oxidised, having transferred all its 4d electrons to the oxygen anions. The 2p state of oxygen is delocalised in the valence region, from -5.5 to 0 eV.



Figure 6.7. Projected density of states (PDOS) for the stoichiometric FeNbO4.

The electronic structure of FeNbO₄ doped at the Fe site with first-row transition metal atoms is depicted in Figure 6.8. It is noteworthy that in the Ti-, V- and Cr-doped structures, the t_{2g} valence orbitals of the dopants progressively shift into the delocalised valence band region. In the Ti- and V-doped structures, we observe only one localised t_{2g} orbital below the Fermi level, while in the Cr- to Ni-doped structures, most 3d states are distributed in the valence region from -6 eV to 0 eV. The PDOS of the Co- and Ni-doped structures indicate that the t_{2g} and e_g orbitals are situated near -7 eV, with the

empty e_g orbitals appearing in the conduction band. Our simulations suggest that with an increase in the atomic number of the dopant, the t_{2g} and e_g orbitals gradually become fully occupied from Cr to Ni, corresponding to the electronic occupations of Ti_{t2g1}^{eg} , V_{t2g11}^{eg} , Ce_{t2g111}^{eg} , Mn_{t2g111}^{eg1} , $Co_{t2g11111}^{eg11}$ and $Ni_{t2g11111}^{eg11}$. Additionally, we found that after doping with Mn, Co or Ni, acceptor levels comprising t_{2g} and e_g orbitals are generated between the VBM and the CBM of the parent material. Generally, doping proves beneficial in reducing the band gap, especially for the structure containing Ti on the Fe site, where the Fermi level is close to the CBM, in agreement with experimental findings.[10] The impact of dopants on the PDOS of Fe, Nb and O is negligible with respect to the parent material.



Figure 6.8. Projected density of states (PDOS) of FeNbO₄ doped with (a) Ti, (b) V , (c) Cr , (d) Mn , (e) Co and (f) Ni on the Fe site.

Our calculations show that when Ti and V are doped into the Nb site of the stoichiometric structure, there are no bands in the valence region, as these cations lack electrons. In the Cr- and Mn-doped structures, the t_{2g} and e_g orbitals appear in the valence band region, but due to the incomplete occupation of 3d orbitals we still observe states in the conduction band region. With increasing atomic numbers, the electrons in the 3d orbitals of Co- and Ni-doped structures tend to occupy states further towards -7 eV. In addition, we found that substituting Nb with Cr, Co, and Mn creates the acceptor levels that are generated above the Fermi level. In all the structures, the 3d orbitals of Fe, 4d orbitals of Nb and 2p orbitals of O show a similar distribution to the parent structure, indicating that the effect of doping on the intrinsic ions is minimal and can be disregarded.



Figure 6.9. Projected density of states (PDOS) of FeNbO4 doped with (a) Ti , (b) V , (c) Cr , (d) Mn , (e) Co , and (f) Ni , on the Nb site.

6.5 Non-stoichiometric o-FeNbO₄

Next, we introduced one oxygen vacancy into the supercells and subsequently again incorporated first-row transition metal dopants into the Fe and Nb sites to investigate their effect on the geometric and electronic properties. Figure 6.10 illustrates four distinct configurations of the O-deficient FeNbO4 structure, *i.e.* when the oxygen vacancy is surrounded by (*i*) three Fe (FFF), (*ii*) two Fe and one Nb (FFN), (*iii*) one Fe and two Nb (FNN), and (*vi*) three Nb (NNN) cations. However, we observed that the NNN type oxygen vacancy migrated and transformed into the FNN type following optimization.



Figure 6.10. Optimised structures of four distinct oxygen vacancy types in the FeNbO₄ structure: (a) FFF; (b) FFN; (c) FNN and (d) NNN. The star denotes the selected doping sites; O is red, Fe is brown and Nb is green.

The lattice parameters of the O-deficient structures are presented in Table 6.7. Our calculations reveal that the introduction of oxygen vacancies induces an expansion in the lattice parameters *a*, *b*, and *c*. The most significant expansions in *a* and *c* are observed in the FNN-vacancy type structure, while the largest expansion in *b* is found in the FFN-vacancy type structure. Moreover, a slight distortion in the crystal shape is noted, with all angles deviating from 90°, particularly γ , which exhibits the largest difference of 0.59° in the FFN-vacancy type structure, see Table 6.7. The enlarged lattice parameters and distorted cell shape collectively contribute to a volume expansion in the structure. This expansion can be rationalised by considering the larger size of

Fe²⁺ compared to Fe³⁺ cations when the latter undergo reduction upon the formation of an O vacancy, as reported in previous studies.[203, 204] The formation energy of the oxygen vacancy was calculated as: $E_{vac} = E_{Fe_{16}Nb_{16}O_{63}} - E_{Fe_{16}Nb_{16}O_{64}} + \frac{1}{2}E_{O_2}$, where $E_{Fe_{16}Nb_{16}O_{63}}$ and $E_{Fe_{16}Nb_{16}O_{64}}$ represent the total energies of the O-deficient FeNbO₄ and stoichiometric FeNbO₄, respectively, and E_{O_2} refers to the total energy of the oxygen molecule in the triplet ground state. The calculated vacancy formation energies indicate that the process is endothermic for the three types of vacancies considered in this study, ranging between 2.14 eV for FFF and 4.13 eV for FNN. This suggests that the material will not spontaneously undergo reduction. The FNN-type vacancy exhibits the largest volume expansion, consistent with its higher number of surrounding Nb atoms. The decreasing order of formation energy for the oxygen vacancies is $E_{vac}^{FNN} > E_{vac}^{FFF} > E_{vac}^{FFF}$.

Table 6.7. Lattice parameters (*a*, *b* and *c*), angles (α , β and γ), volume (*V*) and formation energy of oxygen vacancy (E_{vac}) for the O-deficient FeNbO₄ structure.

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å ³)	<i>∆V/V</i> (%)	Evac (eV)
stoichiometric	9.393	11.367	10.127	90.03	89.93	89.68	1081.339	-	-
FFF	9.409	11.386	10.144	89.94	90.15	89.82	1086.819	0.51	2.14
FFN	9.405	11.383	10.191	90.15	90.27	89.41	1091.086	0.90	3.28
FNN	9.415	11.405	10.180	89.99	89.83	90.17	1093.294	1.10	4.13

6.5.1 Bulk properties

First, we considered the substitutional doping of one Fe cation surrounding the O vacancy in the FFF-, FFN- or FNN-vacancy type structures, as shown in Figure 6.10. The calculated magnetic moment, valence state of the first-row transition metal dopant

and the doping energy released upon substitution of the structural Fe ion are listed in Table 6.7. Our simulations indicate that the magnetic moment decreases to ~3.70 μ_B in only two Fe cations in the three types of structures as a result of the formation of the oxygen vacancy. We observe that two 1st NN Fe ions of the oxygen vacancy have a smaller magnetic moment in the FFF and FFN-type structures, whereas one 1st and one 2nd NN cation experience a reduction in the magnetic moment in the FNN-type structure. Although underestimated, the calculated magnetic moment of ~3.7 μ_B corresponds to an electronic distribution of $Fe_{t2g\uparrow\downarrow\uparrow\uparrow}^{eg\uparrow\uparrow\uparrow\uparrow}$ for an octahedral Fe²⁺, as shown in Figure 6.11.



Free ions

Octahedral field

Figure 6.11. Octahedral field splitting for the 3d orbitals of Fe²⁺.

We found that Ti has the smallest magnetic moment of ~0.80 $\mu_{\rm B}$ of all the dopants considered in this chapter, where the magnetic moments increase with atomic number of the transition metal from Ti to Mn, which has the largest value of ~4.57 $\mu_{\rm B}$. Our calculations also suggest that the magnetic moment decreases from Mn to Co and from Co to Ni. The electronic distributions of $Ti \frac{eg}{t2g\uparrow}$, $V \frac{eg}{t2g\uparrow\uparrow}$, $Cr \frac{eg\uparrow}{t2g\uparrow\uparrow\uparrow\uparrow}$, $Mn \frac{eg\uparrow\uparrow}{t2g\uparrow\uparrow\uparrow\uparrow}$, $Co \frac{eg\uparrow\uparrow}{t2g\uparrow\downarrow\uparrow\uparrow\uparrow}$ and $Ni \frac{eg\uparrow\uparrow}{t2g\uparrow\uparrow\uparrow\downarrow\downarrow\uparrow\downarrow}$ correspond to the valence states +3, +3, +2, +2,

+2 and +2, respectively, see APPENDIX B. It is worth noting that the Cr, Mn, Co, and Ni dopants maintain the same oxidation state as the substituted Fe had before doping of the O-deficient structure. Replacing Fe by Mn and Ni dopants is an energetically favourable process compared to introducing Ti, V, Cr and Co dopants, displaying the following decreasing order of doping energies $E_{Ti} > E_V > E_{Cr} > E_{Co} > E_{Mn} >$ E_{Ni} . The analysis of the magnetic moments suggests that Fe gains one electron, reducing its valence state from 3+ to 2+, upon the formation of the O vacancy in the stoichiometric material, as shown in Table 6.4 and 6.8. The calculated magnetic moments and valence states of the transition metal dopant atoms are essentially the same in the three types of O-deficient structures. Moreover, we found that the magnetic moments and electronic structures of the dopant atoms are very similar in both Fe0.9375A0.0625NbO4 and Fe0.9375A0.0625NbO3.9375, with the exception of the Cr and Mn dopants. The calculated magnetic moment increases from 2.91 to \sim 3.6 u_B and from 3.85 to $\sim 4.5 u_B$ for Cr and Mn, respectively, suggesting that the formation of the O vacancy reduces these cations from the 3+ to the 2+ oxidation state. Only Cr and Mn display a larger magnetic moment, corresponding to a reduction from 3+ to 2+ with respect to the doped material without O vacancies, in agreement with the charge of the Fe²⁺ that they substituted. However, Ti and V, which have a valence state of 3+ donated one electron to the 1st or 3nd NN Fe cations. The doping energy for Ti, V, Cr and Mn (Co and Ni) decreases (increases) from the FFF to the FFN and from the FFN to the FNN type O-deficient structure. Our calculated doping energies suggest that replacing Fe with Ti^{3+} and V^{3+} is thermodynamically less favourable than doping with the other cations in the 3+ oxidation state. We found that the total energy differences ($E_t = E_{vac} + E_{doping}$) between the stoichiometric and doped O-deficient materials are still larger for the FNN-type structure, with the exception of the Ti-doped phase, indicating that doping and partial reduction cannot enhance its stability with respect to the FFF and FFN type structures.

			FFN (Fe site)				FNN (Fe site)					
A	<i>m</i> _s (µ _B)	VS	E_d (eV)	$E_t(eV)$	<i>m</i> _s (µ _B)	VS	E_d (eV)	$E_t(eV)$	m_s (μ_B)	VS	E_d (eV)	E_t (eV)
Fe 1st neigh	3.73 (2)	+2	-	-	3.72(2)	+2	-	-	3.7 (1)	+2	-	-
Fe 3rd neigh	-	-	-	-	-	-	-	-	3.73(1)	+2		-
Ti	0.84	+3	3.72	5.86	0.82	+3	3.31	6.59	0.80	+3	2.01	6.14
V	1.89	+3	1.53	3.67	1.86	+3	1.39	4.67	1.84	+3	1.28	5.41
Cr	3.60	+2	0.91	3.05	3.60	+2	0.76	4.04	3.57	+2	0.68	4.81
Mn	4.57	+2	-0.28	1.86	4.56	+2	-0.32	2.96	4.55	+2	-0.34	3.79
Со	2.75	+2	0.27	2.41	2.71	+2	0.35	3.63	2.74	+2	0.36	4.49
Ni	1.74	+2	-0.79	1.35	1.70	+2	-0.68	2.60	1.73	+2	-0.55	3.58

Table 6.8. Atomic magnetic moments (m_s), valence states (VS), and doping energy (E_d) in equations 6 and energy differences (E_t) of the O-deficient FeNbO4 structure with dopants in the Fe site.

Next, we introduced dopants on the five-fold Nb sites in proximity to the oxygen vacancies and subsequently relaxed the structures before computing their properties, as detailed in Table 6.9. The FFF-type vacancy structure was not considered for Nb site doping due to the absence of a 1st NN Nb site. Our simulations indicate that magnetic moments remain zero for all Nb atoms within the FFN and FNN-type vacancy structures. The magnetic moment of the dopants progressively increases with atomic number from Ti to Mn, while it decreases from Mn to Ni. The magnetic moment configurations for the first-row transition metal atoms correspond to $Ti \frac{eg}{t2g}$, $V \frac{eg}{t2g1}$, $Cr \frac{eg}{t2g1111}$, $Mn \frac{eg1}{t2g11111}$, $Co \frac{eg1}{t2g111111}$ and $Ni \frac{eg111}{t2g111111}$. We have inferred valence states of

+4 for Ti, +4 for V, +3 for Cr, +3 for Mn, +1 for Co and +1 for Ni. Our calculated doping energies reveal that the insertion of Ti, V, and especially Cr and Co into the Nb sites is thermodynamically more difficult than the incorporation of Mn and Ni, with exothermic doping energies of approximately -0.7 and -0.25 eV, respectively. Generally, the generation of oxygen vacancies does not alter the magnetic moment, electronic structure, or oxidation state of Nb⁵⁺ in FeNbO_{3,9375} compared to FeNbO₄. The magnetic moments and oxidation states of the dopants are comparable in both the FFN and FNN-vacancy type structures of $FeNb_{0.9375}B_{0.0625}O_{3.9375}$, but different from the values reported for FeNb_{0.9375} $B_{0.0625}O_4$, except for Ti and Ni. Specifically, the formation of the oxygen vacancy in the doped material leads to changes in the magnetic moments of V, Cr, Mn and Co from 0 to 1 μ_B , 1.60 to ~2.90 μ_B , 3.03 to ~3.80 μ_B , and 2.59 to $\sim 2.0 \mu_B$, respectively, corresponding to a reduction of their oxidation states from +5 to +4, +4 to +3, +4 to +3 and +2 to +1, respectively. Furthermore, we observed that the oxidation state of each dopant is smaller than that of the removed Nb⁵⁺ ion. For instance, the 1+ cations received one electron from each Fe²⁺ and one electron from two 2nd NN O atoms, whereas the 4+ and 3+ cations received charge density from one or two Fe^{2+} ions, respectively. We found that Mn and Ni are the only dopants that can be inserted spontaneously into both the Fe and Nb sites, with Mn displaying a larger preference for the Nb position and Ni for the Fe site. Ti and V are thermodynamically more favourable to dope into the Nb than the Fe site for each vacancy-type structure, whereas Cr and Co preferentially substitute Fe rather than Nb. The largest total energy difference for $FeNb_{0.9375}B_{0.0625}O_{3.9375}$ was calculated for the FNN-type structure, suggesting that doping is unable to modify the order of stability of the doped O-deficient materials.

		FFN	(Nb site)	FNN (Nb site)					
A, B	<i>m</i> _s (µ _B)	VS	E_d (eV)	$E_t(eV)$	m_s (μ_B)	VS	E_d (eV)	$E_t(eV)$	
Nb	0	+5	-	-	0	+5	-	-	
Ti	0	+4	0.27	3.55	0	+4	0.38	4.51	
V	1.00	+4	0.4	3.68	1.00	+4	0.79	4.92	
Cr	2.92	+3	5.47	8.75	2.91	+3	4.76	8.89	
Mn	3.89	+3	-0.78	2.50	3.84	+3	-0.65	3.48	
Co	2.04	+1	5.91	9.19	2.09	+1	5.32	9.45	
Ni	1.47	$^{+1}$	-0.26	3.02	1.45	$^{+1}$	-0.24	3.89	

Table 6.9. Atomic magnetic moments (m_s), valence states (VS), and doping energy (E_d) of the O-deficient FeNbO4 structure with dopants incorporated into the Nb site.

6.5.2 PDOS

Here, we discuss the PDOS of ions proximate to the oxygen vacancy within the intrinsic structures. In the FFF-vacancy type configuration, we selected the three Fe ions, positioned as the 1st NN to the O vacancy at approximately 2.0 Å, and the five Nb atoms, situated as the 3rd NN within the range of 3.2 to 4.0 Å, see Figure 6.12. In the FFN-vacancy type arrangement, we focused on the two Fe and the sole Nb cations, serving as the 1st NN of the O vacancy at around 2.0 Å. For the FNN-vacancy type structure, we considered the lone Fe and the two Nb ions, constituting the 1st NN of the O vacancy at approximately 2 Å. The PDOS was plotted utilising the twelve O anions from the three vacancy-type structures (2rd NN of the O vacancy between 2.6 and 3.4 Å) as well as the three Fe and two Nb ions from the FFN- and FNN-vacancy type structures (3rd NN of the O vacancy between 3.4 and 4.4 Å), to plot the PDOS, shown in Figures 6.12.



Figure 6.12. The 1st (a), 2nd(b) and 3rd (c) NN ions of the oxygen vacancy selected for the PDOS in the FFF-vacancy type structures (a-c); the FFN-vacancy type structures(d-f) and the FNNvacancy type structures (g-i); O is red, Fe is brown and Nb is green.

Figure 6.13 illustrates that the t_{2g} and e_g levels in the majority spin channel between -8.0 and -1.5 eV are fully occupied for the 1st NN Fe ions of the O vacancy in the FFFvacancy type structure. In the FFN-vacancy type structure, the t_{2g} and e_g orbitals of the 1st NN Fe are distributed in the majority spin region from -7 to -1 eV. Our calculations suggest that the minority spin channel remains empty in FeNbO₄ for the 1st NN Fe ions in both the FFF- and FFN-vacancy type structures, with the exception of part of the highly-localised t_{2g} orbital just below the Fermi level. The t_{2g} and e_g states of the 1st NN Fe are located in the majority spin channel, while the orbitals in the minority spin channel are unoccupied in the FNN-vacancy type structure. The majority and minority spin channels of the 3d orbitals of the 1st NN Nb of the O vacancy are symmetric, and their density of states is smaller for the valence than for the conduction band in both the FFN- and FNN-type vacancy structures. We found that the full 2p orbitals of all the 2nd NN oxygen remain delocalised from -7 to -1 eV with respect to the stoichiometric material. For the 3rd NN Nb in the FFF-type vacancy configuration, the negligibly occupied 3d states appear from -7 to -1 eV, whereas the localised states are above 1.0 eV, similar to the FFN- and FNN-type structures. Our simulations indicate that the t_{2g} and e_g levels of the 3rd NN Fe cations are occupied in the majority spin channel in the FFN- and FNN-type vacancy structures. Interestingly, we found that part of the occupied t_{2g} state of the 3rd NN Fe appears highly-localised below the Fermi level in the FNN-vacancy type structure.

Our calculations show that the 1st NN Fe cations of the O vacancy act as donor levels in the FFF- and FFN-type vacancy structures, reducing the bandgap by approximately 1.2 eV compared to the stoichiometric configuration. This behaviour has also been observed in other O-deficient materials such as LaFe_{1-x}Nb_xO₃ and Li₂FeSiO₄.[205-208] Furthermore, we observed that the appearance of donor levels aligns well with the electronic configuration of $Fe: \frac{eg^{\uparrow\uparrow}}{t_2g^{\uparrow\downarrow\uparrow\uparrow\uparrow}}$ for the Fe²⁺ cations. However, the electron in this highly-localised orbital is derived from the 3rd NN Fe in the FNN-vacancy type structure, suggesting a preference for electron conduction in the rather more remote area from the FNN-type vacancy. The absence of localised Fe t_{2g} and e_g states around -8 eV implies the absence of Fe³⁺ in the vicinity of the vacancy sites, specifically in the 1st NN region of the FFN- and FNN-type structures. Our calculations indicate that the 3d electronic states of Nb, regardless of their positions, slightly hybridize with the 2p orbitals of oxygen in the valence band, similar to the stoichiometric FeNbO₄. Consequently, we opted not to discuss their density of states in the subsequent sections.



Figure 6.13. Projected density of states (PDOS) for FeNbO4 with different types of oxygen vacancies (a) FFF; (b) FFN and (c) FNN.

First, we have simulated the PDOS for Fe_{0.9375}A_{0.0625}NbO_{3.9375} structures, containing FFF-, FFN-, and FNN-type vacancies, respectively. We found that the electronic states of the dopants and Fe cations exhibited similar distributions in the three types of oxygen-vacancy structures, see APPENDIX C.1-2. In this context, we chose to analyse

only the PDOS of the doped FFF-vacancy type configuration to investigate the effect of dopants on the electronic structures.

Figure 6.14 illustrates that the 3d orbitals of the 1st NN Fe occupy the majority spin channel from -8 to -1 eV, while the minority spin channel remains unfilled above 1 eV in all the doped structures. Electronic states of Ti, V, and Co dopants are primarily distributed in the conduction region, with one, two and four sharp orbitals, respectively, appearing below the Fermi level. The majority spin channel of the Mn dopant is fully occupied, while its minority spin channel is in the conduction region. The t_{2g} and e_g levels of the Co and Ni dopants are present in both the majority and minority spin channels in the valence region, and part of the conduction band remains unoccupied over 1 eV. In general, our simulations reveal that the highly-localised states of Fe²⁺ below 0 eV are replaced by the t_{2g} orbitals of the Ti, V, and Cr dopants, reducing the band gap to less than 0.5 eV, especially for the Ti- and V-doped structures. In contrast, the t_{2g} and e_g levels of the Mn, Co, and Ni dopants shift towards the deep region of the valence band, resulting in no states around the Fermi levels, consistent with observations in doped TiO₂ as well. [209, 210] The gradual increment of states in the valence region and the decrease of states in the conduction band from Ti to Ni corresponds well with the electronic configurations of $Ti: e_{t2q\uparrow\uparrow}^{eg}$, $V: e_{t2q\uparrow\uparrow\uparrow}^{eg}$, $Cr: e_{t2q\uparrow\uparrow\uparrow\uparrow}^{eg\uparrow}$, $Mn: e_{2g\uparrow\uparrow\uparrow}^{eg\uparrow\uparrow}, Co: e_{2g\uparrow\downarrow\uparrow\downarrow\uparrow}^{eg\uparrow\uparrow}$ and $Ni: e_{2g\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow}^{eg\uparrow\uparrow}$, respectively. Overall, comparing with the doped Fe_{0.9375}A_{0.0625}NbO₄ structures, we observe that the electronic states of Ti and V remain similarly allocated in both doped configurations. On the other hand, the highlylocalised orbitals of Cr and Mn are generated below the Fermi levels in the O-deficient structures. The electronic states of the Co and Ni dopants tend to be delocalised in the valence region from -7 to -1 eV in the $Fe_{0.9375}A_{0.0625}NbO_{3.9375}$ structures, rather than being concentrated around -8 eV in the $Fe_{0.9375}A_{0.0625}NbO_4$ configurations.



Figure 6.14. Projected density of states (PDOS) for dopants and the 1st nearest neighbour (NN) Fe in the FFF-type Fe_{0.9375}A_{0.0625}NbO_{3.9375} structures featuring (a) Ti, (b) V, (c) Cr, (d) Mn, (e) Co, and (f) Ni dopants on the Fe site.

We also selected the PDOS of the FFN-type $FeNb_{0.9375}B_{0.0625}O_{3.9375}$ materials to illustrate their electronic structures, see Figure 6.15, as they exhibit similar distributions to the FNN-type, see APPENDIX C.3-5 We observe that the occupied states of the Fe cations are distributed from -8 to -1 eV for the Ti- and V-doped structures, and from -8 to 0 eV for the Cr-, Mn-, Co- and Ni-doped structures. The t_{2g} and e_g levels of the Ti and V dopants predominantly occupy both the majority and minority spin channels in the conduction region, except for the localised t_{2g} orbitals of V near the VBM. Additionally, our calculations reveal that after substituting Cr, Mn, Co, and Ni into the Nb sites, both the majority and minority spin channels of the valence region are gradually filled by the 3d electrons of the dopants. Specifically, a sharp level is observed in the CBM of the Cr-doped structure, and this type of highly-localised orbitals shifts towards the Fermi levels with an increase in atomic numbers from Cr to Ni. In general, our calculations demonstrate the removal of highly-localised orbitals of the Fe cations below the Fermi levels in the Ti- and V-doped structures. Moreover, we found no evidence of Fe²⁺ in the Cr-, Mn-, Co- and Ni-containing structures, indicating that it has been oxidized back to Fe³⁺ after doping. Furthermore, acceptor levels are generated and tend to move close to the Fermi levels in the Cr- to the Ni-doped structures. During this process, we observe a reduction in the bandgap to 0.5 eV for the Co-doped structure, while it remains relatively large at -1.8 eV for the Cr- and Ni-doped structures, even exceeding that of the undoped O-deficient structures. When comparing with the $FeNb_{0.9375}B_{0.0625}O_4$ structure, we found that the electronic states distributions of Ti dopants remain the same, whereas the additional localised levels of V dopants are situated in the VBM after the generation of oxygen vacancies. The acceptor level, composed of the 3d orbitals of Cr tends to move towards the CBM after the creation of oxygen vacancies. For the Mn-, Co-, and Ni-doped configurations, the impact of the oxygen vacancy on the electronic structures of the dopant is negligible and can be disregarded.



Figure 6.15. Projected density of states (PDOS) of the dopants, the 1st and 3rd nearest neighbour (NN) Fe in the FFN-type Fe0.9375A0.0625NbO3.9375 structures with (a) Ti, (b) V, (c) Cr, (d) Mn, (e) Co, and (f) Ni dopants on the Nb site.

6.6 Chapter conclusion

We have conducted DFT calculations of the Fe_{0.9375} $A_{0.0625}$ NbO₄ and FeNb_{0.9375} $B_{0.0625}$ O₄ materials, where A, B = Ti, V, Cr, Mn, Co and Ni, as well as the O-deficient Fe_{0.9375} $A_{0.0625}$ NbO_{3.9375} and FeNb_{0.9375} $B_{0.0625}$ O_{3.9375} structures (A, B = Ti, V, Cr, Mn, Co and Ni). Our calculations indicate that substituting the Fe cation with these dopants is considerably more energetically favourable than the Nb site, leading to significant compression of FeNb_{0.9375} $B_{0.0625}$ O₄, except for the Ti-doped configuration. Doping Ti, V, and Mn at the Fe site of the stoichiometric structure transforms it into an n-type semiconductor, while the Co- and Ni-doped FeNb_{0.9375} $B_{0.0625}$ O₄ structures shift to p-

type semiconductors.

In the O-deficient structure, a random distribution of cations occurs, resulting in the identification of three stable types of oxygen vacancies, *i.e.* FFF-, FFN-, and FNN-type vacancies. Our calculations have shown that the stability of O-deficient configurations depends on the number of 1st NN Nb atoms at the O vacancy. For instance, generating the FFF-type vacancy is less endothermic than the FNN-type vacancy, leading to the largest volume expansion. Overall, for the doping process in the Fe or Nb sites surrounding the vacancies, we observe that the type of oxygen vacancies does not significantly affect the structural properties and electronic structures of the dopants. However, the presence of an oxygen vacancy can alter the oxidation state and doping energies relative to the Fe_{0.9375}A_{0.0625}NbO₄/FeNb_{0.9375}B_{0.0625}O₄ structures. For instance, the order of doping energies in the Fe sites of the non-vacancy configurations is as follows: $E_{Ti^{3+}} > E_{Co^{2+}} > E_{Ni^{2+}i} > E_{V^{3+}} > E_{Mn^{3+}} > E_{Cr^{3+}}$, whereas in the Odeficient structures, the sequence becomes: $E_{Ti^{3+}} > E_{V^{3+}} > E_{Cr^{2+}} > E_{Co^{2+}} >$ $E_{Mn^{2+}} > E_{Ni^{2+}}$. Furthermore, it is noteworthy that doping Ti and V into the Fe sites of the O-deficient structures could significantly enhance electronic conduction by moving the donor levels close to the CBM. However, doping these first-row transition metals into the Nb site surrounding the vacancies tends to shift the structures towards p-type semiconductors, especially for the Co-doped configurations, where the bandgap narrows from 1.0 to 0.5 eV

Chapter 7: Conclusion and future work

7.1 Conclusion

In this thesis, we have conducted a computational study of the bulk and surface properties of m/o-FeNbO₄, reactions of hydrogen and water molecules with the pristine surfaces, dominant phases of the o-FeNbO₄, diffusion of oxygen in the o-FeNbO₄ supercells as well as the effect of dopants on both the stoichiometric and non-stoichiometric o-FeNbO₄ structures to evaluate these materials for use as fuel electrodes of SOCs.

In the first part (Chapter 3), fundamental research has been carried out on the m-FeNbO4, structure. We found that the calculated lattice parameters show typical monoclinic characteristics with special angle β deviating from 90°. The most stable magnetic structure of m-FeNbO4 shows antiferromagnetization, in good accordance to the experimental results. The simulated electronic structures indicate that m-FeNbO4 is semiconductor structure with a band gap of ~2.0 eV, where electrons are conducted through the Fe-O-Fe networks. In addition, we have investigated the surface properties of seven low-index surfaces of m-FeNbO4 and found that the four surfaces, *i.e.* (010) (011) (110) and (111) surfaces, dominates in the equilibrium morphology. For the surface reactions with water molecules, we found that the most thermodynamically favourable sites for the adsorption of water are the Nb site of the (111) surface and the Fe site of the (011) surface, whereas the dissociation of water on the Fe and Nb sites of the (110) surface have the smallest energy barriers with no more than 0.27 eV at 0 K. Overall, the research work in chapter 3 theoretically demonstrated that the FeNbO₄ materials can be used as the SOECs fuel electrode.

As some experimental work has validated that the SOFCs with o-FeNbO₄ as anode show good performance under hydrogen atmosphere, we have therefore simulated the process of the reduction of hydrogen at the o-FeNbO4 anode side. To mimic a real surface with random distribution of cations, we have generated three (010) surfaces with termination, respectively and one (111) surface in chapter 4. We found that the dissociation of hydrogen are thermodynamically favourable especially at the oxygen bridge sties surrounded by Fe cations. The analysis of Bader charge indicates that the hydrogen atoms coordinated by metal were negatively charged while other atoms in the O-H group have positive Bader charges. Then, we have investigated the formation of water and found that the migration of hydrogen from O-H side requires larger energy than from Fe-H side. The comparison of the energy barriers with other reported anodes, *i.e.* CeO₂ and Ni-YSZ anode demonstrated that. After desorption of the formed water molecules, there appear oxygen vacancies on the surfaces which are filled by the oxygen atoms from electrolyte or bulk side of anodes.

In chapter 5, we have succeeded to investigate the diffusion behaviour of oxygen in the bulk structure of o-FeNbO₄. Before the simulation of diffusion, we have first confirmed
that there is only one dominate phase in the stoichiometric structures, whereas once generating oxygen vacancies in the structure there occurs other dominant phases, which can explain why the real nonstoichiometric o-FeNbO₄ is a disordered structure. For the direct diffusion pathway of the interstitial oxygen in the stoichiometric structure, we found the lowest and largest energy barriers along the [001] direction. We have added the simulation of the pathway of the interstitial mechanism along the [001] direction and found that its energy barrier is larger than the direct diffusion pathway, which can be explained by the strong bond length of Fe/Nb-O. For the nonstoichiometric structure, our simulations indicate that the diffusion of oxygen through the hoping mechanism requires much less energy than the stoichiometric structures and this barrier depends on the type of vacancies along the diffusion pathway.

Finally, to improve the bulk properties, we have introduced the first-row transition metals, *i.e.* Ti, V, Cr, Mn, Co and Ni, into the Fe and Nb sites of both the stoichiometric and nonstoichiometric o-FeNbO₄ reported in chapter 5. We discussed the effect of dopants on the bulk and electronic properties. In the stoichiometric structure doping those atoms into Nb sites generally leads to the compression of volume, compared to the substitution in the Fe sites which is more energetically favourable than the Nb site. Generally, the doping energy can be lowered through generating oxygen vacancies for the substitution in the Nb site, whereas doping Ti, V and Cr into the Fe site of O-deficient requires larger energies than the stoichiometric structure. The electronic structures of those doped phases are modified with respect to the undoped structures and band gaps are narrowed to ~0.5 eV, especially for the Ti and V dopants in the Fe

sites and the Co dopant in the Nb sites.

The research presented in this thesis aims to provide an in-depth understanding to the mechanism of surface reactions with hydrogen and vapour, oxygen diffusion and dopants' effect. We hope that this comprehensive and systematic work are able to be a guide tool for the future theoretical and experimental research on FeNbO₄ and other ABO₄ materials.

7.2 Future work

In chapter 3 and 4, we are concentrated on the dissociation of water and hydrogen for the m- and o-FeNbO₄ phases, respectively. Based on the experimental evidence where both m- and o-FeNbO₄ can be used as the cathode of SOECs or the anode of SOFCs, it would be interesting to investigate the dissociation of hydrogen and water on the surfaces of m- and o-FeNbO₄, respectively to explore how the terminations of surface affect those reactions. In chapter 5, we have discussed the diffusion of oxygen in the o-FeNbO₄ bulk model structure. Future studies on the oxygen surface-bulk exchange would be of great interest to understand its diffusion mechanism in the surface models. In chapter 6, the effect of dopants on the o-FeNbO₄ bulk phase is clear and a final further work is to modify the surface properties by adding dopants on the top and subtop layers of the pristine surfaces of the o-FeNbO₄ structure to predict which substitution would lower the energy barriers of the migration of hydrogen and the formation of gas water.

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Appendix A

Table A.1. Zero point energy (E_{ZPE}) for adsorbates (*H₂O or *OH + *H) from initial state (IS) to transition state (TS) and final state (TS) in the Fe and Nb adsorption sites of (010), (011), (110) and (111) surfaces

	IS (eV)	TS (eV)	FS (eV)
010-Fe site	0.545	0.511	0.509
011-Fe site	0.533	0.524	0.506
011-Nb site	0.534	0.512	0.474
110-Fe site	0.506	0.498	0.447
110-Nb site	0.528	0.520	0.517
111-Fe site	0.566	0.505	0.505
111-Nb site	0.517	0.501	0.473

	IS (eV)	TS (eV)	FS (eV)
010-Fe site	0.096	0.093	0.095
011-Fe site	0.098	0.096	0.095
011-Nb site	0.089	0.087	0.087
110-Fe site	0.079	0.079	0.077
110-Nb site	0.122	0.102	0.071
111-Fe site	0.112	0.110	0.102
111-Nb site	0.076	0.070	0.067

Table A.2. Vibrational entropy (TS) for adsorbates (*H2O or *OH + *H) at 300 K from initial state(IS) to transition state (TS) and final state (TS) in the Fe and Nb adsorption sites of (010), (011),(110) and (111) surfaces.

	IS (eV)	TS (eV)	FS (eV)	
010-Fe site	0.197	0.194	0.195	
011-Fe site	0.200	0.198	0.197	
011-Nb site	0.182	0.181	0.180	
110-Fe site	0.162	0.162	0.159	
110-Nb site	0.250	0.229	0.152	
111-Fe site	0.229	0.226	0.215	
111-Nb site	0.155	0.149	0.145	

 Table A.3. Vibrational entropy (TS) for adsorbates (*H2O or *OH + *H) at 600 K from initial state (IS) to transition state (TS) and final state (TS) in the Fe and Nb adsorption sites of (010), (011), (110) and (111) surfaces

Appendix B



Figure B.1. Octahedral field splitting for the 3d orbitals and the corresponding electron occupation of dopants on the Fe site in the FFF-type O-deficient structure.



Figure B.2. Octahedral field splitting for the 3d orbitals and the coresponding electron occupation of dopants on the Fe site in the FFN-type O-deficient structure.



Figure B.3. Octahedral field splitting for the 3d orbitals and the corresponding electron occupation of dopants on the Fe site in the FNN-type O-deficient structure.



Figure B.4. Octahedral field splitting for the 3d orbitals and the corresponding electron occupation of dopants on the Nb site in the FFN-type O-deficient structure.



Figure B.5. Octahedral field splitting for the 3d orbitals and the corresponding electron occupation of dopants on the Nb site in the FNN-type O-deficient structure.
Appendix C



Figure C.1. Projected density of states (PDOS) for the dopants and the 1st nearest neighbour (NN) Fe in the FFF-type Fe0.9375A0.0625NbO3.9375 structures with (a) Ti , (b) V , (c) Cr , (d) Mn , (e) Co and (f) Ni dopants on the Fe site.



Figure C.2. Projected density of states (PDOS) for the dopants and the 1st and 3rd nearest neighbour (NN) Fe of the FFN-type Fe_{0.9375}A_{0.0625}NbO_{3.9375} structures with (a) Ti , (b) V , (c) Cr , (d) Mn , (e) Co and (f) Ni dopants on the Fe site.



Figure C.3. Projected density of states (PDOS) for the dopants and the 3rd nearest neighbour (NN) Fe of the FNN-type Fe_{0.9375}A_{0.0625}NbO_{3.9375} structures with (a) Ti , (b) V , (c) Cr , (d) Mn , (e) Co and (f) Ni dopants on the Fe site.



Figure C.4. Projected density of states (PDOS) for the dopants and the 1st and 3rd nearest neighbour (NN) Fe of the FFN-type Fe_{0.9375}A_{0.0625}NbO_{3.9375} structures with (a) Ti , (b) V , (c) Cr , (d) Mn , (e) Co and (f) Ni dopants on the Nb site.



Figure C.5. Projected density of states (PDOS) for the dopants and the 1st and 3rd nearest neighbour (NN) Fe of the FNN-type Fe_{0.9375}A_{0.0625}NbO_{3.9375} structures with (a) Ti , (b) V , (c) Cr , (d) Mn , (e) Co , and (f) Ni dopants on the Nb site.