Moybdenum based materials synthesis and energy applications

Xiao, Peng

2015

Xiao, P. (2015). Moybdenum based materials synthesis and energy applications. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/65076>

<https://doi.org/10.32657/10356/65076>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**MOLYBDENUM BASED MATERIALS
SYNTHESIS AND ENERGY APPLICATIONS**

XIAO PENG

SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING

2015

MOLYBDENUM BASED MATERIALS SYNTHESIS AND ENERGY APPLICATIONS

XIAO PENG

School of Chemical and Biomedical Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2015

Acknowledgements

During the four years in Nanyang Technological University, I have truly experienced the excitement of enrolment and envision of research life, the depression from failures of experiments, and the ecstasy out of acceptance of publications. Towards the end period of the graduate-student life or even being a student, when looking back to my undergraduate, I seem feel that I grew from a maverick undergraduate to now, a ready candidate for Ph.D, not only in learning professional skills in lab, academic writing for publication, but also gaining insights for tackling an issue. This process is not easy, likening a roughly-cut log shaping out for furniture, which is cutting, chiselling, and remoulding. And it really needs guiders or mentors. I have a group of people around, and help me through this. Here, I acknowledge them.

Firstly, it is my supervisor, professor WANG Xin. It is him who gave me an opportunity to study in Singapore four years ago, a freed platform – the lab where I could put ideas and thoughts into practice, unlimited mentoring, guidance towards the final work – publications, and sometimes courageous words. If I hadn't the chance Prof. Wang Xin gave me, I would have been in lost for longer, and my career would have been more detoured. I am grateful to Professor Wang xin, and if all the work I have done might be an honour, this honour is to him.

Secondly, I would thank Dr. GE Xiaoming, my senior in a collaborative lab. It is him who practically introduces me into research, experiments in manual, which is fundamental and precious to me. I express my great gratitude to Dr. GE Xiaoming for his advices, discussion, even sometimes mentoring me.

Thirdly, I thank my group members: Dr. XIA Baoyu, Dr. LI Nan, YAN Ya, WANG Haibo, ZHENG Lulu, XIE Mingshi, Larrisa THIA, ZHOU Huiming, LIM Rern-jern.

I also thank Dr. Mahasin Alam Sk for the support in DFT calculation, and Dr, WANG Xiujuan, a technician who has given and been giving valuable advices and professional trainings for SEM, TEM, XRD *etc.*.

Last but the most important, I would thank my family, especially my mother for her selfless love and invaluable support throughout all the years. Besides, I would like to give my thankfulness to my girlfriend Louisa Tsang, and thank her for her accompany during my Ph.D.

Table of contents

Acknowledgements	0
Table of contents	1
List of Figures	4
List Of Abbreviations	8
List of Tables	9
Abstract.....	10
Chapter 1 Introduction and literature review	13
1.1 Introduction	13
1.1.1 Hydrogen economy	13
1.1.2 Utilization of H_2 in fuel cells.....	15
1.1.3 Production of hydrogen	21
1.2 Literature review	25
1.2.1 Solid oxide fuel cells	25
1.2.1.1 $La_{1-x}Sr_xCr_{1-y}Mn_yO_{3-\delta}$ (LSCM)	26
1.2.1.2 Molybdenum based perovskite material	29
1.2.2 Electrochemical production of H_2	32
Molybdenum/tungsten disulfide, chalcogenides	32
Carbides.....	40
Phosphides.....	42
Others.....	45
1.3 Objectives of the thesis	46
Chapter 2 H_2 and CH_4 oxidation on $Gd_{0.2}Ce_{0.8}O_{1.9}$ infiltrated $SrMoO_3$–yttria-stabilized zirconia anode for solid oxide fuel cells.....	48
2.1. Introduction	48
2.2. Experimental	49
2.3. Results and discussion	51
2.3.1. Characterization of $SrMoO_3$ -YSZ anode in H_2 oxidation	51
2.3.2. Effect of GDC infiltration on H_2 oxidation	54
2.3.3 Redox cycling stability test for GDC infiltrated $SrMoO_3$ -YSZ anode	56
2.3.4 Influence of water content on cell performance in H_2 oxidation	58
2.4. Conclusions	60
Chapter 3 $Sr_{1-x}Ca_xMoO_3$–$Gd_{0.2}Ce_{0.8}O_{1.9}$ as the anode in solid oxide fuel cells: effects of Mo precipitation	61

3.1. Introduction	61
3.2. Experimental	63
3.2.1. Materials synthesis.....	63
3.2.2 Materials characterization.....	63
3.2.3 Fuel cell test.....	63
3.3. Results and discussion	64
3.3.1 Metal Mo segregation on $Sr_{1-x}Ca_xMoO_3$ and the structure analysis.....	64
3.3.2 Reversibility examination of Mo ex-solution	70
3.3.3 Anode structure analysis and its electrochemical performance towards H_2 and CH_4	73
3.4. Conclusions	74
Chapter 4 Investigation of molybdenum carbide nano-rod as an efficient and durable electrocatalyst for hydrogen evolution in acid and alkaline	76
4.1. Introduction	76
4.2. Experimental	77
4.2.1. Mo_2C nano-rods synthesis	77
4.2.2. Material characterization	78
4.3. Results and discussion	80
4.3.1. Phase transition from molybdenum complex to Mo_2C nano-rod and its morphology	80
4.3.2. Electrochemical, conductivity test	82
4.4. Conclusions	92
Chapter 5 Synthesis and electrochemical activation of molybdenum tungsten carbide nanowires for efficient and stable hydrogen evolution.....	93
5.1. Introduction	93
5.2. Experimental	95
5.2.1 Materials and methods.....	95
5.2.2 Materials characterization.....	95
5.2.3 Measurements of the weight ratio in the binary carbides.....	96
5.3. Results and discussion	97
5.4. Conclusions	112
Chapter 6 Molybdenum phosphide as an efficient electrocatalyst for hydrogen evolution reaction	113
6.1. Introduction	113
6.2. Experimental	115
6.2.1 Materials synthesis and methods	115

6.2.2 Materials characterization.....	115
6.2.3 Electrode preparation and electrochemical measurements.....	115
6.2.4 Computational Methods and Models	116
6.3. Results and Discussion.....	121
6.4. Conclusions	133
Chapter 7 Conclusions and Perspectives.....	134
References.....	136

List of Figures

Figure 1 - 1 Schematic illustration of working mechanism for fuel cell	18
Figure 1 - 2 Schematic illustration of photocatalytic process with photosensitizer and seperated catalyst.	23
Figure 1 - 3 A, B site in perovskite structure coordinated by O	25
Figure 1 - 4 Performance with $(\text{La}_{0.75}\text{Sr}_{0.25})_{0.9}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ as the anode under wet hydrogen condition (3 wt.%). Reprinted with the permission from Ref.[92]. Copyright 2003 Nature Publication Group.	27
Figure 1 - 5 Therotical calculation of Gibbs free energy of H adsorption on catalysts. Reprinted with permission from Ref. [125]. Copyright (2005) American Chemical Society.	32
Figure 1 - 6 ‘Volcano plot’ of the exchange current density vs. Gibbs free energy. Reprinted with permission from Ref. [126]. Copyright (2007) The American Association for the Advancement of Science	33
Figure 1 - 7 2H-MoS ₂ structure viewed (a) in <i>c</i> direction; (b) on <i>ab</i> plane.	35
Figure 1 - 8 1T-MoS ₂ structure (a) <i>c</i> direction; (b) perspective <i>ab</i> plane;(c) illustration of octahedral site Mo occuppies.....	35
Figure 1 - 9 schematic illustration of a solvothermal route for synthesis (A) MoS ₂ /rGO; (C) MoS ₂ . SEM images of (B) MoS ₂ /rGO; (D) aggregated MoS ₂ particles. Reprinted with permission from Ref. [134]. Copyright (2010) American Chemical Society.	36
Figure 1 - 10 Schematic model for the synthesis of double gyroidal MoS ₂ (DG MoS ₂). Reprinted with the permission from Ref. [149]. Copyright 2012 Nature Publication Group	39
Figure 1 - 11 Nanostructured Ni ₂ P particle for HER (A) LSV scan in 0.5 M H ₂ SO ₄ ; (B) Tafel Plot of Ni ₂ P and Pt; (C) TEM image of as-synthesized Ni ₂ P nano particles. Reproduced with permission from Ref. [205]. Copyright (2013) American Chemical Society.....	42
Figure 2 - 1 XRD patterns (a) synthesized SrMoO ₄ ; (b) standard SrMoO ₄ PDF card; (c) GDC infiltrated SrMoO ₃ -YSZ; (d) SrMoO ₃ -YSZ anode; (e) SrMoO ₄ -YSZ...52	52
Figure 2 - 2 Impedance spectra for H ₂ oxidation at 800 °C on SrMoO ₃ -YSZ anodes with different weight ratio.....	53
Figure 2 - 3 surface morphology for different SrMoO ₃ -YSZ anodes: (a) SrMoO ₃ (90 wt.%)/YSZ; (b) SrMoO ₃ (70 wt.%)/YSZ; (c) SrMoO ₃ (50 wt.%)/YSZ; (d) GDC infiltrated SrMoO ₃ (50 wt.%)/YSZ.	53
Figure 2 - 4 Impedance spectra at 800 °C on SrMoO ₃ (50 wt.%)/YSZ (diamond), 14 wt.% GDC infiltrated SrMoO ₃ (50 wt.%)/YSZ (rectangle), 56 wt.% GDC infiltrated SrMoO ₃ (50 wt.%)/YSZ (circle) in H ₂ /3% H ₂ O and their fitted results using an equivalent circuit shown below.....	54
Figure 2 - 5 Overpotential for different amount of GDC loading on SrMoO ₃ (50 wt.%)/YSZ anode at 800 °C in H ₂ /3% H ₂ O	56

Figure 2 - 6 Redox stability test at 900 °C on single cell GDC, SrMoO ₃ -YSZ YSZ LSM-YSZ, (a) I-V-P curves; (b) impedance spectra under open circuit voltage.....	57
Figure 2 - 7 Cross section view (a) fresh cell; (b) after 5 redox cycles test;.....	58
Figure 2 - 8 (a) I-V-P curve for dry and wet H ₂ oxidation at 900 °C and (b) their EIS curves, respectively under OCV condition.	59
Figure 3 - 1 XRD pattern of (a) SrMoO ₄ ; (b) Sr _{0.7} Ca _{0.3} MoO ₄ ; (c) Sr _{0.5} Ca _{0.5} MoO ₄	65
Figure 3 - 2 XRD patterns of (a) SrMoO ₃ ; (b) Sr _{0.7} Ca _{0.3} MoO ₃ ; (c) Sr _{0.5} Ca _{0.5} MoO ₃	66
Figure 3 - 3 Rietveld Method on (a)SrMoO ₃ ; (b)Sr _{0.7} Ca _{0.3} MoO ₃ ; (c) Sr _{0.5} Ca _{0.5} MoO ₃ . 67	
Figure 3 - 4 Structure visualization of (a) and (b) for SrMoO ₃ and Sr _{0.7} Ca _{0.3} MoO ₃ (in cubic Pm3m); (c) and (d) for Sr _{0.5} Ca _{0.5} MoO ₃ (in tetragonal I4/mcm) ((c) and (d) are in view of c direction).	68
Figure 3 - 5 Morphological graph by FESEM: (a) Sr _{0.5} Ca _{0.5} MoO ₃ –GDC; (b) Sr _{0.7} Ca _{0.3} MoO ₃ –GDC; (c) Sr _{0.5} Ca _{0.5} MoO ₄ –GDC; (d) SEM image for cross-section view of a single cell	69
Figure 3 - 6 XRD patterns of (a) fresh prepared Sr _{0.5} Ca _{0.5} MoO ₄ ; (b) Sr _{0.5} Ca _{0.5} MoO ₃ obtained by reducing fresh prepared Sr _{0.5} Ca _{0.5} MoO ₄ ; (c) Sr _{0.5} Ca _{0.5} MoO ₃ obtained after a redox cycle (the cycle to oxidize Sr _{0.5} Ca _{0.5} MoO ₃ to Sr _{0.5} Ca _{0.5} MoO ₄ and then reduce back)	70
Figure 3 - 7 XRD patterns of (a) Sr _{0.7} Ca _{0.3} MoO ₄ ; (b) Sr _{0.7} Ca _{0.3} MoO ₃ ; (c) Sr _{0.7} Ca _{0.3} MoO ₃ after one redox cycle; (d) re-oxidized Sr _{0.7} Ca _{0.3} MoO ₄ from (c).	71
Figure 3 - 8 (a) TGA-DTA curves of Sr _{1-x} Ca _x MoO ₃ oxidation and the DSC curves are assigned accordingly in colours; (b) MoO ₃ TGA in black squares and its DSC in red line (peaks of rising-up denoting exothermic, dropping-down as endothermic, indicated by pink arrows).....	72
Figure 3 - 9 (a) I-V-P curves for Sr _{0.5} Ca _{0.5} MoO ₃ –GDC SrMoO ₃ –GDC anodes at 800 °C in H ₂ ; (b) their corresponding EIS curves.	74
Figure 4 - 1 calibration of saturated calomel electrode in (a) 0.5 M H ₂ SO ₄ and (b) 1 M KOH.	79
Figure 4 - 2 XRD patterns of molybdates: a) 450 °C, pure H ₂ ; b) 600 °C, pure H ₂ ; c) 700 °C, pure H ₂ ; d) 700 °C, 50 vol.% H ₂ /Ar; e) 700 °C, 35 vol.% H ₂ /Ar; f) 700 °C, 20 vol.% H ₂ /Ar.	80
Figure 4 - 3 FESEM images (a) HMo-Mo ₂ C-R; (b) LMo-Mo ₂ C-R.	81
Figure 4 - 4 Morphology of Mo ₂ C-R (a) FESEM images; (b, c, d) TEM images.	82
Figure 4 - 5 XPS of (a) Mo ₂ C-R; (b) HMo-Mo ₂ C-R	83
Figure 4 - 6 Raman spectrum of Mo ₂ C-R and HMo-Mo ₂ C-R.....	83
Figure 4 - 7 Conductivity measurements of as-synthesized Mo ₂ C-R.....	84
Figure 4 - 8 Polarization curves in 0.5 M H ₂ SO ₄ , mass loading 0.43 mg cm ⁻²	85

Figure 4 - 9 Tafel plots of commercial Mo ₂ C, Mo ₂ C-R, HMo-Mo ₂ C-R, LMo-Mo ₂ C-R, 20% Pt/C in 0.5 M H ₂ SO ₄	86
Figure 4 - 10 Bode plots in 0.5 M H ₂ SO ₄ under different overpotentials: (a) HMo-Mo ₂ C-R; (b) LMo-Mo ₂ C-R	87
Figure 4 - 11 EIS curves in 0.5 M H ₂ SO ₄ : (a) Nyquist plot and (b) Bode plot of Mo ₂ C-R; (c) Nyquist plots of LMo-Mo ₂ C-R and Mo ₂ C-R at $\eta=150$ mV; (d) Nyquist plots of LMo-Mo ₂ C-R, Mo ₂ C-R and their fitting results at $\eta=200$ mV.....	87
Figure 4 - 12 Randles' circuit as the equivalent model.....	88
Figure 4 - 13 Stability test of Mo ₂ C-R in 0.5 M H ₂ SO ₄ , scanning rate: 100 mV s ⁻¹	89
Figure 4 - 14 Polarization curves of various catalysts in 1 M KOH solution.	90
Figure 4 - 15 (a) 10 wt.% Ni loading on Mo ₂ C-R; (b) 30 wt.% Ni loading on Mo ₂ C-R	91
Figure 5 - 1 morphology of synthesized (a) WO ₃ nanowire; (b) nw-W ₄ MoO ₃ ; (c) nw-W ₄ MoC; (d), (e), (f): TEM images of nw-W ₄ MoC; (g) Mo K α 1, and (f) W L α 1: TEM-EDX mapping with respect to the area in (f).....	97
Figure 5 - 2 SEM graph of nw-W ₂ MoO ₃	98
Figure 5 - 3 SEM images of nw-W ₂ MoC	99
Figure 5 - 4 SEM image of WC	99
Figure 5 - 5 BET surface area of nw-W ₄ MoC.....	100
Figure 5 - 6 XRD of (a) WC.; (b) Mo ₂ C; (c) nw-W ₂ MoC; (d) nw-W ₄ MoC.	100
Figure 5 - 7 XPS of nw-W ₄ MoC sample: before activation (a) Mo 3d; (b) W 4f; (c) C 1s; After electrochemcal activation (d) C1s.....	101
Figure 5 - 8 polarization curves of molybdenum tungsten carbide (scan rate: 2 mV/s): (a) before CV activation, (c) after CV activation; Tafel plots: (b) before CV activation, (d) after CV activation.....	103
Figure 5 - 9 TGA of nw-W ₂ MoC and nw-W ₄ MoC	104
Figure 5 - 10 Bode and Nyquist plot of nw-W ₄ MoC at different over-potentials in 0.5 M H ₂ SO ₄	106
Figure 5 - 11 Raman spectra of nw-W ₄ MoC.....	107
Figure 5 - 12 polarization curve by cyclic voltammetry at different potential window, (a) 0.26 V to 0.46 V vs. RHE; (b) 0.26 V to 0.61 V vs. RHE in 0.5 M H ₂ SO ₄	108
Figure 5 - 13 XPS of nw-W ₄ Mo, C1s electron, after cyclic voltammetry activation from 0.26 V to 0.46 V vs. RHE in 0.5 M H ₂ SO ₄	109
Figure 5 - 14 XPS of nw-W ₄ MoC activated from 0.26 V to 0.61 V vs. RHE: (a) Mo 3d; (c) W 4f; nw-W ₄ MoC activated from 0.26 V to 0.46 V: (b) Mo 3d; (d) W 4f.	109
Figure 5 - 15 polarization curve by cyclic voltammetry at different potential window, (a) 0.26 V to 0.61 V vs. RHE; (b) 0.26 V to 0.8 V vs. RHE in 0.5 M H ₂ SO ₄	110
Figure 5 - 16 stability test of nw-W ₄ MoC in 0.5 H ₂ SO ₄ with an inset graph showing chronoamperometric electrolysis	111

Figure 5 - 17 polarization curve of freshly activated electrode and aged electrode ...	111
Figure 6 - 1 Top view of (a) (110)-Mo and (b) (001)-MoP, Mo terminated surfaces; It shows the binding sites for H adsorption (only the first two atomic layers are shown. Mo – cyan sphere, P – magenta sphere).	118
Figure 6 - 2 Top view of H adsorbed (110)-Mo, (001)-MoP, Mo and P terminated surfaces. Only first two atomic layers are shown.	119
Figure 6 - 3 XRD patterns of (a) Mo; (b) Mo ₃ P; (c) MoP.	121
Figure 6 - 4 schematic graph to show the structural evolution upon phosphorization	122
Figure 6 - 5 Morphology of MoP (a) FE-SEM and (b) TEM graph.	122
Figure 6 - 6 bulk Mo ₃ P materials synthesized at 800 °C under Ar	123
Figure 6 - 7 EDS of as-synthesized (a) MoP and (b) Mo ₃ P. The calculated atomic ratios of Mo: P from EDS are 0.645/0.657 and 0.69/0.21.	123
Figure 6 - 8 X-ray photoelectron spectra (XPS) of the as-synthesized MoP (a) Mo 3d and (b) P 2p; aged MoP (c) Mo 3d and (d) P 2p.	124
Figure 6 - 9 XRD pattern of aged MoP	124
Figure 6 - 10 MoP after electrochemical test (c) Mo 3 d and (d) P 2p	125
Figure 6 - 11 (a) Polarization curves of Mo, Mo ₃ P and MoP in 0.5 M H ₂ SO ₄ , scan rate: 2 mV s ⁻¹ ; (b) Tafel plots in 0.5 M H ₂ SO ₄ ; Electrochemical impedance spectra of MoP: (c) in 0.5 M H ₂ SO ₄ and (d) in 1 M KOH.	126
Figure 6 - 12 Bode plot of MoP: (a) in 0.5 M H ₂ SO ₄ ; (b) 1 M KOH	130
Figure 6 - 13 (a) polarization curve before and after durability test, scan rate: 2 mV s ⁻¹ ; (b) chronoamperometric electrolysis;.....	131
Figure 6 - 14 SEM graphs for before/after stability test	132

List of Abbreviations

H ₂ ICEs	hydrogen fuelled internal combustion engines
PEMFC	Proton exchange membrane fuel cell
PAFC	Phosphoric Acid Fuel Cell
AFC	alkaline Fuel Cell
MCFC	Molten Carbonate Fuel Cell
SOFC	Solid Oxide Fuel Cell
PTFE	Polytetrafluoroethylene
ECSA	electro-chemical surface area
CHP	Combined Heat and Power
IT-SOFC	Intermediate temperature solid oxide fuel cell
YSZ	Yttrium stablized zirconia
LSM	Lanthanum strontium manganite ($\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$)
LSGM	Lanthanum strontium gallate mangesite oxide ($\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_3$)
SDC	Samarium doped ceria
GDC	Gadolinium doped ceria
LDC	Lanthanum doped ceria
ORR	Oxygen reduction reaction
HER	Hydrogen evolution reaction
MIEC	Mixed ionic and electronic conductivity
SFM	Strontium iron molybdate ($\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$)
rGO	Reduced graphene oxide
DMF	Dimethylformamide
HDS	Hydrodesulfurization
XPS	X-ray photoelectron spectroscopy

List of Tables

Table 1 - 1 Properties of PEMFC, PAFC, AFC, MCFC, SOFC.....	17
Table 1 - 2 Electrochemical reactions, electrolytic ion for typical fuel cells	17
Table 3 - 1 Refinement results and crystallographic data for SrMoO_3 , $\text{Sr}_{0.7}\text{Ca}_{0.3}\text{MoO}_3$ and $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_3$ at room temperature	68
Table 4 - 1 Tafel slope b, exchange current density j_0 in 0.5 M H_2SO_4	88
Table 4 - 2 Tafel slope b, exchange current density j_0 in 1 M KOH.....	91
Table 5 - 1 Tafel slope b and exchange current density j_0	105
Table 5 - 2 charge transfer resistance of nw-W4MoC before and after cyclic voltammetry	105
Table 6 - 1 Calculated binding energy (eV) of single H atom on (110)-Mo and (001)- MoP surfaces	118
Table 6 - 2 Calculated binding energy and Gibbs free energy of H adsorption on (110) Mo and (001) MoP, Mo and P terminated surfaces	120
Table 6 - 3 Calculated binding energy and Gibbs free energy of H adsorption on (001) Mo ₃ P, P terminated.	127
Table 6 - 4 Tafel slope b and exchange current density j_0	129
Table 6 - 5 Fitting data of EIS of MoP in 0.5 M H_2SO_4 and 1 M KOH	130

Abstract

The content of this thesis includes most of my research work during my Ph.D., and it is categorized into two aspects— hydrogen oxidation and hydrogen production. Together with hydrogen transportation/storage, they are central to hydrogen economy. To realize hydrogen economy for the future, we aim to develop non-noble, cost-effective catalysts for efficient and stable hydrogen oxidation and production. The body of this thesis consists of 6 chapters: the first chapter is background introduction and literature review; the second and third are for hydrogen oxidation in SOFC; the last three chapters are the summary of electrochemical hydrogen production by using molybdenum based non-noble catalysts, including porous Mo_2C rods, binary $\text{Mo}_2\text{C}/\text{WC}$ nanowires, and bulk MoP.

Adopting the electrode configuration of the state-of-the-art Ni based anode, *e.g.*, Ni–YSZ and the concept of full-ceramic anode, *e.g.* $\text{Sr}_2\text{M}_{1-x}\text{Mo}_x\text{O}_{6-\delta}$, we propose to use highly conductive SrMoO_3 ($\sim 10^3 \text{ S cm}^{-1}$ [1]) to replace Ni, forming a composite anode with YSZ. Concerning the catalytic activity of pristine SrMoO_3 –YSZ anode, different mass loadings of GDC were infiltrated. Regarding the improved performance for hydrogen oxidation, various characterizations are applied, *e.g.* EIS, linear polarization, and potentiostatic test *etc.*, to examine its redox cycling stability, influence of water content in H_2 for optimal power output.

Subsequently, in chapter 3, dopant calcium is used to partially substitute for Sr in the A site of perovskite structure, forming a catalyst of $\text{Sr}_{1-x}\text{Ca}_x\text{MoO}_3$ for hydrogen oxidation in SOFCs. Structural destabilization is evoked by Ca substitution, causing Mo ex-solution on the surface of host anode $\text{Sr}_{1-x}\text{Ca}_x\text{MoO}_3$ –GDC. Characterizations, *e.g.* XRD and TGA, are employed to have verified the reversibility of Mo ex-solution,

which ensures $\text{Sr}_{1-x}\text{Ca}_x\text{MoO}_3$ –GDC anode good redox cycling stability. Analysis through the Rietveld method to refine XRD data reveals that structure evolution is responsible for the ex-solution of metal Mo. The Mo ex-solution boosts the performance of H_2 oxidation at 800 °C, achieving 330 mW cm^{-2} compared to 280 mW cm^{-2} for SrMoO_3 –GDC.

For hydrogen production, we firstly synthesized porous Mo_2C rods with different loadings of metal Mo *via* the route of anisotropic growth of anilium trimolybdate. The investigation of electrochemical activity and measurement of conductivity show that porous Mo_2C rod is an excellent catalyst for HER both in acidic and alkaline media, and possesses high conductivity ($\sim 30 \text{ S cm}^{-1}$). It is also found that nano-sized metal Mo on the surface has negative contribution to the performance, and Ni-impregnated porous Mo_2C rods exhibit nearly zero onset potential in alkaline, like Pt. Then, we integrated Mo_2C with WC in a nanowire structure. The electrochemical test results indicate that cyclic voltammetry scans (0 to 0.63V vs. RHE) would induce a hydrophilic interface that leads to much enhanced performance in catalysing HER in acid. We employ XPS, TEM coupled EDX, to characterize the binary nanowire, and find that the high activity for HER is ascribed to the features of high conductivity because of WC, well-dispersed Mo_2C nano particles as the active sites, and electrochemically induced carboxyl interface.

Finally, we adopt MoP, a good catalyst for HDS. For the first time, we intuitively examine its activity of HER in acid. The results of electrochemical tests suggest that even bulk MoP performs well in catalysing HER. Experimental investigation of the catalytic activity of metal Mo, Mo_3P , and MoP points out that the degree of phosphorization plays an important role in making a good catalyst for HER.

Theoretical study attests that phosphorus site in MoP functions as a ‘hydrogen deliverer’, achieving zero Gibbs free energy at certain H coverage, and is responsible for the high performance obtained for HER in both acid and alkaline.

Chapter 1 Introduction and literature review

1.1 Introduction

1.1.1 Hydrogen economy

Hydrogen is the lightest element in periodic table. Its molecular form, H_2 is able to generate the highest energy per unit weight among common fuels, *e.g.* hydrocarbons, without carbon emission. This carbon-neutral energy carrier is proposed as a promising substitution for fossil fuels [2] in this century, and the system that delivers energy using hydrogen gives rise to the term-hydrogen economy. The initiation of hydrogen economy in modern society started from a report by John Brokris in 1970 [3]. Since then, the development of hydrogen economy, involving its production, transportation, and end use, burgeoned [4-7]. Unfortunately, to date, hydrogen is still far from the market acceptance as the major energy source. Regardless of the underdevelopment of the technology for hydrogen storage that mainly relies on compression to liquid form under high pressure cryogenically [8-10] in high capital, the major use (59% [11] or nearly half) of the produced H_2 is surprisingly for the synthesis of ammonium, which is directly or indirectly used as fertilizer [12]. The other half the H_2 is serving the oil industry by converting heavy petroleum to on-board use of gasoline. The primary means for the utilization of H_2 in a green way, free of carbon emission is proposed as hydrogen-fueled internal combustion engine and fuel cells.

A direct substitution H_2 for fossil fuel in internal-combustion engine gives hydrogen-fuelled internal combustion engine (H_2 ICEs), which is envisaged a promising future with intrinsic advantages over that fueled by gasoline. Apart from the lowest molecular weight that gives the highest energy output per unit weight, the high diffusivity relative to gasoline and wide range of flammability enable high-quality governing of

the throttling without pumping loss [13] because of the easy mixture of fuel with air/O₂ in wide options of ratios. Besides, it achieves lower level of NO_x emission or even zero emission if lean operation is adopted [14], higher thermal efficiency (43.37% vs. 35.74% for gasoline engine [15, 16]) compared to gasoline engines. Several paradigms were shown in the demonstration of H₂ICEs powered microbus [17], forklift [18]. However, the drawbacks and limitations are equally exposed after it is made into on-board use products, including the innate abnormal combustions (pre-ignition, backfire, knock *etc.*), which are even more severe than gasoline engine due to the low flammability of H₂. Comparative studies of H₂ICEs and gasoline engine show an inferior peak power output of H₂ICEs, below 83% [19, 20] or only 50% [21] relative to gasoline engine, and this problem is highly correlated with the extremely low volumetric power density.

An advanced power generation system is needed, which satisfies high conversion efficiency, power output, while achieving environment-friendly, zero emission of greenhouse gas and nitrogen oxides (NO_x). Fuel cells with all aforementioned characteristics emerge as promising devices for future. This device works beyond the mechanism of Carnot cycle (adopted by internal combustion engines), free of the constraint by Carnot principle, and they directly converts chemical energy to electricity in high efficiency, and reversely store remaining energy from intermittent, unevenly distributed sources (*e.g.* solar, wind energy) to valuable chemicals/energy carriers. In addition to high reversibility, fuel cells are of high scalability, built in the size of a central power plant to distributed household power supply, and even portable devices for daily use. Given this, fuel cells are about to be a major form in hydrogen economy in the future.

1.1.2 Utilization of H₂ in fuel cells

Fuel cell can be traced back to 1830s' by a German chemist Christian Friedrich Schönbein and a Wels Physicist William Grove [22-24]. Their initiative model engenders modern technology of fuel cells. Up to date, five primary types of fuel cells are well developed – Polymer Electrolyte Membrane Fuel (PEM), Phosphoric Acid Fuel Cell (PAFC), Alkaline Fuel Cell (AFC), Molten Carbonate Fuel Cell (MCFC) and Solid Oxide Fuel Cell (SOFC) with their properties summarized in table 1-1. Being distinguished from internal combustion engine, fuel cells undergo through a different route, where chemical reactions of fuel, oxygen/air happen individually in anode, cathode, separated by electrolyte. Anode where fuel is oxidized, thus is charged negative with electron flowing *via* external circuit to cathode; Cathode where oxygen/air is reduced, thus is charged positive. In this process, electrolyte delivers charges in the forms of mobile ions, *e.g.* H⁺, O²⁻, which is determined by the type of the charge carrier of the electrolyte used. For the five prototypes of fuel cells, their work mechanism is shown in Figure 1-1, and their specific electrochemical reactions are list in Table 1-2.

1.1.2.1 Proton exchange membrane fuel cell (PEMFC)

PEMFC, as reflected by its name, essentially consists of a membrane that only allows proton to pass through (*i.e.* H⁺) and anode, separated with cathode typically that are composed of Pt as the catalysts uniformly scattering on carbon paper/cloth. Its working environment (electrolyte) is acid at the temperature ranging from 50 to 100 °C. By adopting noble metals as the catalyst, PEMFC has achieved impressive

performance as an energy device. When operating on hydrogen, it reaches the power density of 1.35 kW/liter compared to 0.06 kW/liter for AFC [25]. It is also reported that PEMFC powered vehicles can accelerate from 0 to 97 km/h in less than 16 s, reaching a top speed of 135 km/h [26]. However, the major obstacle for its commercialization is the high production cost due to using noble catalyst. Efforts have been made, and will continue to focus on the reducing the use of Pt, thus rendering PEMFC as a more competitive, efficient and cost-effective device. They are lying in following aspects: (1) synthesis of nano-structured Pt to maximize the ECSA; (2) Pt-M [27] (M= Co [28, 29], Ni [30], Cr, V [31], Fe [32], Cu [33, 34]) alloys to expose the most active crystal surface while stabilized by M; (3) novel catalysts developing to replace Pt; (4) combined strategy 1 and 2. On the other hand, the state-of-the-art Nafion membrane holds high protonic conductivity (~ 0.1 S/cm) as well as high price, so that not only further lessening ohmic loss is needed by improving its conductivity, cost-reduction should be persistently pursued. In the past decades since it drew attentions, the catalyst loading has reduced significantly from 30 – 40 mg/cm² to well below 1 mg/cm² [35], and it is anticipated that another factor of 5-10 would be attained by advanced technologies.

1.1.2.2 Phosphoric acid fuel cell (PAFC)

Phosphoric acid fuel cell is one type of PEMFC by using phosphoric acid as the electrolyte [36]. Its configuration is similar to typical PEMFC by using noble metal Pt or its alloys that are highly dispersed on carbon as the electrode where fuels are regulated in channels by bipolar plates. PAFC is firstly built in stack as a model demonstration of PEMFC power plant 1969 by United Technology Corporation (UTC), but towards the end of last century, the development of PAFC is

Table 1 - 1 Properties of PEMFC, PAFC, AFC, MCFC, SOFC

Fuel Cell Type	Operation Temperature	Typical stack size	Efficiency	Advantage	Disadvantage
proton exchange membrane fuel cell (PEMFC)	50 - 100 °C (typical 80 °C)	1kW to 100kW	60%	low corrosion management problem	expensive catalyst sensitive to impurities
phosphoric acid fuel cell (PAFC)	150 - 200 °C	< 400kW module	40%	high tolerance of impurities	long start up time and expensive catalyst
alkaline fuel cell (AFC)	23 - 70 °C	10 —100kW	60%	Low cost components	sensitive to CO ₂
molten Carbonate fuel cell (MCFC)	600 - 700 °C	300 kW module	45% to 50%	high efficiency and fuel flexibility	high corrosion rate at high temperature and long start up time
solid oxide fuel cell (SOFC)	600 - 1000 °C	< 2 MW	60%	high efficiency and suitable for CHP & CHHP	high temperature corrosion and breakdown of components

Table 1 - 2 Electrochemical reactions, electrolytic ion for typical fuel cells

Type of Fuel cells	Anode reaction	Charge carrier	Cathode reaction
PEMFC	$H_2 \rightarrow 2H^+ + 2e^-$	H^+	$1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$
PAFC	$H_2 \rightarrow 2H^+ + 2e^-$	H^+	$1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$
AFC	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$	OH^-	$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$
MCFC	$H_2 + CO_3^{2-} \rightarrow CO_2 + H_2O + 2e^-$	CO_3^{2-}	$1/2O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$
SOFC	$H_2 \rightarrow H^+ + e^-$	H^+	$1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$
	$H_2 + O^{2-} \rightarrow H_2O + e^-$	O^{2-}	$1/2O_2 + 2e^- \rightarrow O^{2-}$

dwindling, which is due to the high cost of large power plant construction. Future researches are proposed to focus on the reduction of Pt use. Technical solutions such as metal alloys are to be adopted, and the same competitive performance of Pt alloys is being pursued. On the another hand, long-term durability still fall short. As suggested by post characterization after operation for 5000 h [37], severe corrosion took place on carbon; recrystallization and aggregation of Pt occurred. Overcoming the drawbacks of PAFC may set an exemplary model for other types of fuel cells

Figure 1 - 1 Schematic illustration of working mechanism for fuel cell

1.1.2.3 Alkaline fuel cell (AFC)

Alkaline fuel cell basically use KOH (30% – 35 wt.%) as the electrolyte, OH^- as the charge carrier in the electrolyte. The non-acid media enables the use of non-noble, earth-abundant metals. Among them, nickel with unique activity in alkaline solution, is chosen for AFC as anode material. The well-developed, state-of-the-art nickel material for electrode is Raney nickel [38, 39]. It is generally prepared by dissolving off aluminium from aluminium-nickel alloys, followed by passivation in air, reactivation through electrochemical processes [40]. Electrode could be made by rolling Raney nickel with PTFE/carbon. To enhance catalytic properties, dopants at a weight ratio of 1 – 3% [41] are incorporated, in binary systems, *e.g.* Ni-Mo [42], Ni-Ti [43], Ni-Cr [44], Ni-Cu [45, 46], and ternary alloys Ni-Mo-Fe *etc.* [47, 48]. The oxygen electrodes adopts silver, which can be prepared similarly to Raney nickel electrode, and achieved equivalent performance as Pt electrode [49].

One critical challenge is to overcome the sensitivity of the electrolyte (alkaline) to CO₂, likely causing precipitation of electrolyte (carbonate) that lowers the ionic conductivity and obstructs porous electrodes. Regarding to the application of AFC in future, its lifetime, reliability, solutions to high cost should be concerned in order to be competitive against combustion engine (US \$150/kW vs. \$400-500/kW for AFC) [25, 40].

1.1.2.4 molten carbonate fuel cell (MCFC)

Molten carbonate fuel cell uses carbonate salts as the electrolyte, *i.e.* CO₃²⁻ as the charge carrier. Several features of MCFC pose itself advantage over other types fuel cells: (1) working at high temperature enables MCFC to adopt non-Pt materials as the electrode, *e.g.* nickel/nickel oxide, which could potentially reduce the cost of unit production; (2) compared to PEMFC and AFC, molten carbonate salt is free of poisoning of CO₂/CO; (3) unlimited to hydrogen fuel, MCFC is able to utilize versatile fuels, *e.g.* biogas, hydrocarbon *etc.*.

Long-term stability is the major concern for MCFC. Poor durability is originated from the severe corrosion of electrode in molten carbonate salt under its work condition. To overcome poor durability and high fabrication cost is key for the advancement of MCFC in future.

1.1.2.5 Solid oxide fuel cell (SOFC)

Solid oxide fuel cell (SOFC) is another device that is able to adopt non-noble metal as electrode materials. The cermet electrode, typically Ni–YSZ, is composed of metal and ceramics formed in physical mixture, of which ceramic provides the oxygen source through conducting oxide ions (O²⁻), and metal, functions as both electrical conductor and catalyst for H₂ adsorption/dissociation. Triple phase boundary (TPB) is formed between them as the reaction sites, where fuel (H₂), electrons, O²⁻ meet. Up to date, the state-of-the-art cermet Ni–YSZ based anode, by adopting an advanced anode-

support cell configuration, achieves high performance in the temperature range of 600 °C ~ 800 °C (intermediate temperature SOFC: IT-SOFC). Generally, the optimized anode support planar single cell that configures, *e.g.*, Ni–YSZ with the anode (800 µm ~ 1mm), ~10 µm YSZ as the electrolyte [50] and LSM–YSZ (~30 µm) as the cathode, achieves ~ 1 W cm⁻² [51-53] in H₂ at 800 °C.

Although researches of stack-cell have advanced to Megawatts, *e.g.* 250 MW [54], the same issue for commercialization encountered by SOFC, likewise the other types of fuel cells, is the high production cost. Bloom Box ES 5000 energy server quotes a 100 kW per unit for 800,000 dollars [55]. Japanese government is still subsidizing household SOFCs setups for boosting the use of clean energy. On the cusp of the commercialization for the SOFC, obstacles are to overcome. Although possessing many advantages, nickel based anode still exhibits shortcomings. Poor redox stability upon the start-up and shutdown evokes a large volume expansion of 69.2 % caused by nickel oxidized nickel oxide [56], and vice versa in volume shrinkage. Large volume change that reaches beyond the tolerance limit of YSZ could lead to cell collapse. High humidity conditions (large current density) inevitably facilitate surface oxidation of nickel, and the low tolerance to fuel impurities (H₂S *etc.*) causes permanent damage to nickel based anodes, thus losing active sites. Those drawbacks of nickel calls forth new anode materials with the challenge to achieve high redox stability, tolerance of sulfur, catalytic activity *etc.*. To face off the challenges, full ceramic materials are proposed for SOFC [57], and they are reviewed in section 1.2.1.

1.1.3 Production of hydrogen

For the realization of hydrogen economy imminently, production of hydrogen is placed at top priority, and the production should be cost-effective and is from renewable and sustainable energy so that the whole cycle by introducing hydrogen is environment-friendly and contributing positively. Globally, approximately 50 billion kilograms of hydrogen per year is consumed, primarily in petroleum refining [58]. To cater for the large consumption, five key production methods are developed, which are steam reforming, biological production (*via* a fermentative process), thermochemical production, photovoltaic assisted water-splitting, electro-chemical production (catalytic electrolysis).

Steam reforming, is a process of oxygenation of carbonaceous species in steam, by which hydrogen in water is freed from oxygen to form hydrogen on catalysts. Various sources *e.g.* methane [59], ethanol [60], glycerol [61] and biomass [58], can be used as the carbon sources. In addition, catalysts as an importance factor, determine the production rates, efficiency, yield. The state-of-the-art catalyst is supported metal Ni that is dispersing on materials with high surface area, such as TiO₂, SAB-15 (mesoporous silica), ZrO₂ *etc.*. By adopting cheap catalysts and widely fetchable carbon source, production of hydrogen from steam reforming is among the means with the lowest cost. Biological production [62] is to utilize the way that bacteria consume organics, *e.g.* glycerol, carbohydrate [63], and inorganics, *e.g.*, sulfur [64, 65]. Through this fermentative process, hydrogen can be yielded. Techniques including dark fermentation, photo-fermentation, continuous/fed-batch fermentation are used. Issues of low yield, bulky reactor, long residence time [66] are to be addressed for cost-effective hydrogen production. Thermochemical production of hydrogen is based on the decomposition of water (steam) at high temperature (It need as high as ~2000 °C for thermolysis of water [67]). In the process of thermolysis, auxiliary chemicals

are added. These added chemicals can integrate hydrogen and/or oxygen to form new chemicals through chemical reactions at high temperature, and released them through reverse reactions at low temperature with the original chemicals reproduced, which is called thermochemical hydrogen/oxygen production. The integration & release cycle is termed thermochemical cycle [68]. By introducing the intermediate chemicals, the decomposition temperature is decreased, *e.g.* $\sim 530\text{ }^{\circ}\text{C}$ *via* Cu-Cl cycle [68] (*vs.* $2000\text{ }^{\circ}\text{C}$ without chemical reaction cycles); the efficiency is enhanced. A typical S-I (sulfur-iodine) cycle successfully works at the temperature of $850\text{ }^{\circ}\text{C}$, and achieves a production rate of 0.065 kg per day [69]. One of the shortcomings of thermochemical production is to construct advanced equipment with high tolerance towards high temperature, and sometimes high acid-corrosion resistance in the case of S-I cycle. Besides, complicated cycles are involved. For example, to separate H_2 and I_2 in S-I cycle, multi-stage procedures are needed [70], and this inevitably increases the cost of equipment, production of hydrogen.

Photovoltaic assisted water splitting for hydrogen production is to utilize the photocatalytic activity of semiconductors or artificial photosynthesis system to harvest solar energy to reduce water, thus producing hydrogen. The overall working mechanism is that based on semiconductor materials with proper band gap, adsorbed incident light excites electron from valence band to conduction band, and the excited electron is free to reach the catalyst surface, which is the active site with the potential low enough (below 0 *vs.* RHE) to reduce proton or equivalently charged hydrogen species to molecular H_2 . The left hole is either consumed by sacrificial reagent or utilized for another half oxidative reaction, *e.g.* oxygen evolution reaction. Well-developed systems typically include TiO_2 and titanate [71-73], Ta and Nb compounds/complex compounds [74, 75], Ga/Ge [76, 77] and other transitional oxide

e.g. WO_6 , sulfides. To break the constraint of semiconductors as the catalysts that require specified band gap and the capability of light adsorption, artificial photosynthesis is proposed [78, 79] by replacing semiconductors with a photosensitizer and molecular catalysts. As shown in Figure 1-2, photosensitizer (PS) undertakes the role of light adsorption, after which PS is reduced to PS^- , and subsequently transfer the electron to catalysts to form Cat^- that further reduce proton or

Figure 1 - 2 Schematic illustration of photocatalytic process with photosensitizer and separated catalyst.

equivalently charged hydrogen species to molecular H_2 . The left oxidized photosensitizer is quenched by sacrificial reagent (Sac). Despite the photocatalytic production of hydrogen is justified as the most promising way by directly using solar energy, green, zero-emission and environmentally friendly, the low conversion efficiency and short lifetime of the catalyst are still the obstacles to be a major route to deliver hydrogen.

Catalytic electrolysis, *i.e.* electrochemical water-splitting is to directly use city electricity to electrochemically convert water to hydrogen and oxygen gas. To realize this, reductive and oxidative reactions are to take place on two separated electrodes to ensure high conversion rate and Faradaic efficiency. Given this, electrode materials are highly critical, and also because of the cheap electrode materials-Ni that is adopted in alkaline electrolysis, alkaline electrolysis is commercialized, up to megawatt [80]. In contrast, in acid, limited options in noble metals are still the obstacles for PEM electrolysis [81], resulting in the high capital cost of systems. Acidic electrolysis for hydrogen production, *e.g.* PEM electrolysis, provides higher proton conductivity (less ohmic loss), lower gas crossover that enables to operate at higher working pressure, and higher current density. These attractive attributes are built on the utilization of platinum-group metals/metal oxides as the catalysts, *e.g.* Pt, iridium oxides. To push the advance of PEM electrolysis for the application of hydrogen production, novel materials at low cost, earth-abundant reservation are explored, and expect to perform as well as Pt-group metals, or at least close to. Recently, non-noble catalysts for HER have increasingly become a prosperous topic, with exciting results reported constantly, and they are reviewed in Section 1.2.2.

1.2 Literature review

1.2.1 Solid oxide fuel cells

Following section 1.1.2.5, this section will give a review of ceramic anode as a substitution for Ni based anode. Ceramic materials have their intrinsic advantages when they are applied to high-temperature fuel cell. In contrast to nickel, they have better compatibility with electrolyte (YSZ/LSGM that is chosen for IT-SOFC), high redox stability with smaller volume expansion, high tolerance of sulfur (impurities in fuels), tunable conductivity and catalytic activity towards anodic reactions. The most outstanding materials family thereof, are perovskite materials.

Perovskite is nominally written as ABO_3 , face-centre cubic (FCC) packed O^{2-} , where larger size cations occupy 12-coordinated A site, *e.g.* Ca, Sr, La, Y, Ce *etc.*, and smaller size cations occupy 6-coordinated B site, such as Fe, Mo, Ni, Co *etc.*, as shown below.

Figure 1 - 3 A, B site in perovskite structure coordinated by O

Perovskite material shows versatile properties, such as dielectric properties, high conductivities and catalytic activities for H₂ or hydrocarbons oxidation. The exemplary demonstrations in SOFC is using (La_{0.75}Sr_{0.25}Cr_{0.5})_{0.9}Mn_{0.5}O₃ and Sr₂MMoO₆ (M = Mg, Mo) [57], and they successfully showcased a full-ceramic SOFC device by adopting perovskite materials, which attains very impressive performance in both H₂ and CH₄. More than just anodic fuel oxidation free of coke in hydrocarbons, they also exhibit excellent oxygen reduction at the temperature of 600 °C to 1000 °C. Those two works widens the scope of exploring novel materials for SOFC, and initiates a burgeoning field – full-ceramic SOFC. Herein, Focus on anode materials, two major series are introduced, namely, La_{1-x}Sr_xCr_{1-y}Mn_yO_{3-δ} (LSCM) and double perovskite molybdate.

1.2.1.1 La_{1-x}Sr_xCr_{1-y}Mn_yO_{3-δ} (LSCM)

Lanthanum strontium manganite (LSM) [82-87] is commonly used as cathode material in SOFC at high temperature (above 800 °C) due to its excellent conductivity and catalytic activity for ORR under oxidizing atmosphere (Mn⁴⁺/Mn³⁺ couple [88] ~ 485 S cm⁻¹ at 1000 °C [89]), but not stable under reducing conditions, which limits its application in anode. (La,Sr)CrO₃ [90, 91] is widely used as the joint material in SOFC stack because of its high stability under both reducing and oxidizing conditions, but performs poorly as the catalyst for fuel oxidation. A break-through discovery is to dope Cr into LSM to form La_{1-x}Sr_xCr_{1-y}Mn_yO_{3-δ} (LSCM) [92] as the anode material. An exciting performance in wet hydrogen was achieved as shown in Figure 1-4, ~ 200 mW cm⁻² at 900 °C. Sequential studies of LSCM anode materials continued, replacing electrolyte with LSGM (higher conductivity), fabrication of compounded anode

with ceria based materials, and selectively dopants into A/B site for structural engineering at lattice level. For example, for the bare LSCM as the anode, 165 mW cm⁻² was reported by Huang et al. [93] under humidified H₂ on LSGM supported cell

Figure 1 - 4 Performance with $(\text{La}_{0.75}\text{Sr}_{0.25})_{0.9}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ as the anode under wet hydrogen condition (3 wt.%). Reprinted with the permission from Ref.[92]. Copyright 2003 Nature Publication Group.

at 850 °C, which still lacks sufficient power output. Apart from the limited conductivity (MIEC) under reducing condition, $\sim 1 \text{ S cm}^{-1}$ [1, 94-96], LSCM anodes are found to be insufficient in catalytically oxidizing fuel at intermediate temperature (below 800 °C) in SOFC. G. Kim *et al.* [97, 98] investigated the catalytic requirement of LSCM as a potential anode, and achieved less than 100 mW cm⁻² on the cell configuration LSCM|YSZ| $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$ (LSF)-YSZ. One solution is to utilize 0.5 wt.% Pd-5 wt. % CeO₂ by infiltration into the LSCM anode, forming nano-structured Pd-CeO₂ as the catalyst, dramatic improvement was observed, up to 1 W cm⁻² under humidified H₂ at 800 °C. This phenomenon implicates that LSCM can form very stable porous anode frame, but requires additional catalyst loaded to ensure high

performance. Apart from Pd-CeO₂, Pd or GDC-impregnated LSCM and LSCM-LDC compounded were examined as potential anodes. With GDC incorporation, GDC-LSCM [99] electrode polarization resistance (R_p) was only 0.12 $\Omega \text{ cm}^2$ at 800 °C in H₂ (3 wt.%). Ding *et al.* [100] reported that an anode supported cell based on LSCM-SDC anode with thin SDC layer as the electrolyte reached a maximum power density (P_{max}) of ~600 mW cm⁻² in wet H₂ at 700 °C.

With the motivation to improve conductivity and catalytic activity of LSCM, doped LSCM were studied [101], such as Ru-LSCM [102], Ce-LSCM [103, 104] *etc.*. A typical study is to substitute a more electrochemically active Ni for Cr on B site, nominal as (La_{0.75}Sm_{0.25})(Cr_{0.5-x}Ni_xMn_{0.5})O_{3-δ} (LSCMNi) by T. Jardiel *et al.* [105]. This study showed improved electrical conductivity of LSCMNi relative to LSCM. It is also found that under reducing condition, Ni nanoparticles ex-solves on the surface of LSCMNi, resulting in enhanced performance in fuel oxidation. Similar phenomenon was observed on Ru-LSCM where nano-scale Ru particles precipitate on the surface of the host material – LSCM, and function as highly active catalyst for anodic reaction [102]. It is proposed that if the ex-solution of metal nanoparticles is reversible upon reducing and oxidizing conditions, highly redox stability would be achieved. The ex-solved metals not only compensate the low conductivity and catalytic activity for LSCM, but also enlighten the way to revitalize the anode by exposing anode to oxidant (air/O₂), and successfully prevent the particle growth in anode [106]. LSCM as host material, being redox stable with low volumetric change, is an ideal candidate for SOFC anode. To advance the development of LSCM based materials, new doping chemistry is to explore.

1.2.1.2 Molybdenum based perovskite material

The study of molybdenum based perovskite materials for SOFC originates from the success of $\text{Sr}_2\text{Mg}_{1-x}\text{Mn}_x\text{MoO}_6$ series that have catalytic oxidation of both H_2 , featuring in high MIEC (10 S cm^{-1}), and high catalytic activity because of Mo (VI/V) redox couple as the catalytic agent [57]. However, $\text{Sr}_2\text{Mg}_{1-x}\text{Mn}_x\text{MoO}_6$ double perovskite families suffer from chemical incompatibility with electrolyte, *e.g.* YSZ, GDC, even not with LSGM. Besides, reducing conditions are required for synthesis to ensure their high activity. To address those issues, strategies have been made, including varieties of dopants on B site, and fabrication of compound anode by incorporating ceria based materials.

Dissolution/substitution elements into/for the B site is a good strategy for tailoring material: aliovalent/isovalent substitution [107] for Mo may introduce oxygen vacancies or increase electronic conductivity, with possible activation of the metal oxygen (M–O) bond. Apart from Mg, Fe as a felicitous dopant to construct $\text{Sr}_2\text{Fe}_{1-x}\text{Mo}_{0.68}\text{O}_{6-\delta}$ was studied. By applying $\text{Sr}_2\text{FeMoO}_6$ directly with LSGM electrolyte without LDC ($\text{La}_{0.6}\text{Ce}_{0.4}\text{O}_2$) as the buffer layer, a performance of 800 mW cm^{-2} in city gas, $\sim 400 \text{ mW cm}^{-2}$ in dry CH_4 was reported by Zhang *et al.* [108, 109]. Unfortunately, $\text{Sr}_2\text{FeMoO}_6$ still can only be synthesized under reducing environment due to its limited solubility of Mo in $\text{SrFeO}_{3-\delta}$ in air, merely $\sim 17 \text{ at.}\%$, namely maximum stoichiometry formula $\text{Sr}_2\text{Fe}_{1.34}\text{Mo}_{0.68}\text{O}_{6-\delta}$ [110]. A break-through work was conducted for realizing iron-rich in double perovskite materials. $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ (SFM) as the potential anode was reported by Liu *et al.* [111, 112]. According to their study, $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ can be obtained in air, which exempts the reducing treatment at the elevated temperature in 5% H_2/Ar , such as SrTiO_3 [113, 114] based material, $\text{Sr}_2\text{FeMoO}_6$ aforementioned, and Sr_2MMgO_6 (M=Mn, Fe, Ni, Co, Zn, Mg) [115] in order to maintain a higher conductivity and pure phase.

The excellent stability and high conductivity under both air and reducing condition, up to 550 S cm^{-1} in air and 310 S cm^{-1} in H_2 respectively, render $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ as a promising material for both anode and cathode for SOFC. On a symmetrical cell using LSGM as the electrolyte, $\sim 800 \text{ mW cm}^{-2}$ was achieved in H_2 . Besides its high redox cycling stability, $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ was attested as a regenerative anode in H_2S -poisoning test.

Built on $\text{Sr}_2\text{Mg}_{1-x}\text{Mn}_x\text{MoO}_6$, La [116], Sm and Al [117], Co [118], Ni [119] have been experimented to substitute for A/B site. Improved electrochemical activities could be achieved, *e.g.* higher electrical conductivity for $\text{Sr}_{2-x}\text{Sm}_x\text{MgMoO}_6$, $\sim 16 \text{ S cm}^{-1}$ (*vs.* 10 S cm^{-1} before dope), when x rises to 0.4 [120]. But, it also comes with negative consequences. For example, segregation of La_2O_3 and formation of SrMoO_4 would take place after annealing $\text{La-Sr}_2\text{MgMoO}_6$ at the temperature ranging from $700 \text{ }^\circ\text{C}$ to $1000 \text{ }^\circ\text{C}$ [120], likewise the segregation of Sm_2O_3 and SrMoO_4 for $\text{Sr}_{2-x}\text{Sm}_x\text{MgMoO}_6$ when $x \geq 0.6$ [121].

Considering the difficulty to accomplish high catalytic activity, high MIEC, incorporation of another material to form compound is a good strategy to optimize the performance of ceramic anodes. SDC incorporation into SFM as anode/cathode was studied [122]. The interfacial R_p decreased to only $0.258 \text{ } \Omega \text{ cm}^2$ in H_2 at $700 \text{ }^\circ\text{C}$. By introducing SDC that possesses high ionic conductivity and electro-catalytic activity, the enhanced oxygen ion exchange and mass transportation [123] result in high performance, and render SDC-SFM promising materials for IT-SOFC. Similarly, in another study, SFM-GDC as the cathode on an anode supported cell, power output higher than 2 W cm^{-2} was reported by Dai *et al.* at $800 \text{ }^\circ\text{C}$ in H_2 [124].

Overall, double perovskite materials, namely Mo based tri-elements complex ceramic that is subject to the formula $\text{Sr}_2\text{M}_{1-x}\text{Mo}_x\text{O}_{6-\delta}$, have the disadvantage of reactivity with

LSGM. To avoid the La inter-diffusion, LDC, SDC or GDC is used as the buffer layer, and to some extent, this tends to be impractical, complicated procedures and evokes higher cost.

Our proposal points to the use of the single form SrMoO_3 , and the justification for using SrMoO_3 and objectives for its application will be discussed in Section 1.3.

1.2.2 Electrochemical production of H₂

Molybdenum/tungsten disulfide, chalcogenides

Water electrolysis in acidic media undergoes a pathway of firstly proton adsorption on catalyst (denoted as Cat in the reactions), followed by combination with electrons to form Cat-H, a bonded atomic hydrogen, and finally integration of two hydrogen atoms to give molecular H₂, released from catalyst with Cat freshly reproduced, as shown below.

Gibbs free energy ($\Delta G^\circ_{\text{H}}$) is used as a ‘descriptor’ to judge the catalyst candidate from thermodynamic perspective, and its value describes the strength of H bound to catalyst. Ideal catalysts should achieve close-to-zero $\Delta G^\circ_{\text{H}}$, which means the catalyst binds H neither too strongly nor too weakly as is the case of Pt, shown in Figure 1-5.

Figure 1 - 5 Theoretical calculation of Gibbs free energy of H adsorption on catalysts. Reprinted with permission from Ref. [125]. Copyright (2005) American Chemical Society.

Pt that achieves close-to-zero $\Delta G^\circ_{\text{H}}$, is referred as a prototype catalyst for HER. In contrast, earth-abundant metals, *i.e.* Ni, Mo, are excluded as good candidates.

Another descriptor, exchange current density, is used to interpret the performance by extrapolating over-potential to zero. By reference to Pt, a ‘volcano plot’ is drawn in a summary of exchange current density for various metals in Figure 1-6.

Figure 1 - 6 ‘Volcano plot’ of the exchange current density vs. Gibbs free energy. Reprinted with permission from Ref. [126]. Copyright (2007) The American Association for the Advancement of Science

Compared to Pt-group metals, cheap metals, Ni, Mo, Co *etc.* exhibit inferior performance in terms of exchange current density and are regarded beyond the consideration for HER, in accordance with $\Delta G^\circ_{\text{H}}$. However, the work by Hinnemann *et al.* [125] and Jaramillo *et al.* [126] reveal that through organic/inorganic ligation of those cheap metals, *e.g.* Ni, Co, Mo *etc.*, their $\Delta G^\circ_{\text{H}}$ can be modified to Pt-resembling level, *i.e.* close to zero, and it means that the binding strength is tunable

by forming compounds. MoS₂ is a successful case by modulating metal molybdenum. More importantly, the length of edges of MoS₂ are correlated with the performance, and imply that by exposing edges, activity could be significantly improved [126]. Sequential studies are conducted in developing new synthesis methods, with the intentions to expose active edges, and overcome the major drawback of MoS₂ – low conductivity. Note that those techniques thereof applying to MoS₂, also work on other sulfide, *e.g.* tungsten disulfide, selenides, and result in a big family of chalcogenides developed as the catalyst for HER. Herein, in the section, we summarize the techniques to improve conductivity, including MoS₂ composites and metallic phase (1T phase); focus on optimal active edges, we reviewed the approaches that include amorphous MoS_x synthesis, dopants into MoS₂, and nano-structured MoS₂ – nanosheet & Gyroidal MoS₂. Beyond the molybdenum/tungsten chalcogenides, substitution of molybdenum sulfide engenders two major non-noble catalysts – carbide (Mo₂C) and phosphides with superiority in both attributes aforementioned, and they are summarized afterwards.

Molybdenum disulfide (nominal MoS₂), is analogous to graphite, a layered material. Bulk MoS₂ is formed *via* van der waals force among layers, and each layer is consisted of the S-Mo-S slab, in the thickness of 6.7 ~ 7 angstroms [127]. In nature, MoS₂ is present in hexagonal pack (2H phase), thermodynamically stable. Figure 1-7 shows the structure of 2H MoS₂, where Mo is 6-coordinated by S atom (Figure 1-7b) with MoS₆ packed in trigonal prism. Viewing from *c* direction reveals a interlayer shift relative to the top layer, indicated by the voids for Mo atoms beneath the top layer in Figure 1-7a. A more important phase for HER is its 1T, metallic MoS₂, as shown in Figure 1-8. Similar to 2H-MoS₂, Mo is 6-coordinated by S, but is in the octahedral site. This

Figure 1 - 7 2H-MoS₂ structure viewed (a) in c direction; (b) on *ab* plane.

change results in a dramatic increase of electrical conductivity, making 1T-MoS₂ a more active catalyst for HER. Jin *et al.* reported a lithium intercalation route for the synthesis of 1T-MoS₂ from as-synthesized multi-layered 2H-MoS₂ [128]. Pronounced improvement of activity of 1T-MoS₂ compared to 2H-MoS₂ is observed,

Figure 1 - 8 1T-MoS₂ structure (a) *c* direction; (b) perspective *ab* plane; (c) illustration of octahedral site Mo occupies.

in lower onset potential, Tafel slope. This strategy is also applicable to WS_2 [129]. Emphasis is given to the reductive reagent butyl-lithium that destabilizes 2H- MoS_2 by transferring abundant electrons, thus changes the density of state, and renders a metastable 1T- MoS_2 [130, 131]. Through a sophisticated chemical exfoliation of bulk MoS_2 , 1T- MoS_2 can be obtained, yet with the co-existence of 2H phase [130], which unequivocally inferiorizes the performance towards HER [131]. Moreover, 1T- MoS_2 is observed to be stable only below 95 °C [132], and even long-term ageing at ambient condition would lead to transition back to 2H phase [133]. Given that 1T- MoS_2 encounters the issue of stability, solely relying on stabilising 1T- MoS_2 may fall short. One solution is to resort to supported MoS_2 , *e.g.* on cheap carbon materials. Dai *et al.* successfully disperse MoS_2 on rGO [134]. As illustrated in Figure 1-9, a solvothermal method in DMF enables a uniform dispersion of MoS_2 nano-plates on reduced graphene, resulting in much enhanced performance.

Figure 1 - 9 schematic illustration of a solvothermal route for synthesis (A) MoS_2/rGO ; (C) MoS_2 . SEM images of (B) MoS_2/rGO ; (D) aggregated MoS_2 particles. Reprinted with permission from Ref. [134]. Copyright (2010) American Chemical Society.

Compared to aggregated MoS_2 particles, MoS_2/rGO achieves a cathodic

current density of $\sim 25 \text{ mA/cm}^2$ while nearly zero for MoS_2 particles at a overpotential of 250 mV. Sequential studies are conducted, including using different Mo/S sources, *e.g.* thiourea [135], MoCl_5 [136] and adopting conductive support [137, 138], *e.g.* MoS_2 supported crumpled graphene balls [139], mesoporous graphene [140]. Via the control of reagent ratios by separating Mo from S (unlike $(\text{NH}_4)_2\text{MoS}_4$ in DMF in Ref. [134]), it attains optimal coverage of MoS_2 with finely engineered edges in layered MoS_2/rGO hybrid [136]. To further enhance the conductivity, tungsten carbide (WC) is incorporated to form a $\text{MoS}_2/\text{WC}/\text{rGO}$ ternary catalyst [141]. Here, WC not only improves the overall electrical conductivity, but also mitigates rGO restacking. Moreover, growth of molybdenum on 3D graphene on the backbone of nickel foam is reported by Li *et al.* [142]. The high performance is attributed to the high conductivity of 3D graphene that is free of oxygen radicals, and nickel foams as the electrode with high MoS_2 loading ($\sim 17 \text{ mg}$ on a geometrical area of $\sim 2 \text{ cm}^2$). In a word, rGO/graphene that is selected as the catalyst support for MoS_2 is based on the features of its high conductivity, large surface area, chemical compatible to MoS_2 that enables the growth of well-defined MoS_2 within a few layers, which contribute tremendously to the activity towards HER compared to bulk MoS_2 , as is the case of WS_2 [143].

Instead of graphene, carbon nanotube (CNT) is also chosen as a support for MoS_2 . Reported studies can be categorized into nano MoS_2 plates/CNT [144], MoS_3 deposited on CNT [145], molybdenum sulfide/N-CNT with/without vertical alignment [146]. Improved performance is observed, and it lies in enhanced conductivity due to the introduction of CNT as well as the well-defined structure, which to a significant extent proliferates the active sites in orders of magnitude. Other catalyst supports including mesoporous carbon nanosphere [147], MoO_3 - MoS_2 in a core-shell nanowire [148] are reported. Those effects are for targeting novel design of a composite catalyst

whereby poor conductive MoS₂ could be integrated onto highly conductive backbones. The as-formed composite is made an excellent catalyst for HER. There is still one point noteworthy that improved performance may not solely arise from enhanced conductivity from the support, but the extended edges formed simultaneously during synthesis. The next part is to focus on the methodology for seeking highly exposed edges for attaining high activity by construction in a well-define nano-structure, *e.g.* nano plates, and amorphous MoS_x.

One example is to construct MoS₂ in Double Gyroidal structure (DG MoS₂) via a sacrificial template route [149]. By controllably prepared in a contiguous thin film in nano structure, it achieves optimal catalytically active sites (the typical synthesis is schematically illustrated in Figure 1-10). More practically, MoS₂/WS₂ assemblies in thin layers can be realized by hydrothermal method in Teflon-lined autoclaves [150-153], solid state reaction [154], chemical vapour deposition (CVD) [155]. It is pointed out that the catalytic activity of MoS₂ is highly correlated with the numbers of layers, and the performance of HER decrease at a factor of 4.4 with increasing an layer [155]. This layer-dependent activity is ascribed to the electron hopping barriers among layers; the exposed active edges are hypothesized to assist the electron hopping. Hence, thin layer with highly exposed edges are pursued. Vertically aligned thin-layer of selenides and sulfides are rendered [156-159]. Via chemical vapour deposition, a rapid selenization/sulfurization process can successfully retain the metastable phase of MoSe₂/MoS₂ that is oriented perpendicular to the substrate, and enables more active

Figure 1 - 10 Schematic model for the synthesis of double gyroidal MoS₂ (DG MoS₂). Reprinted with the permission from Ref. [149]. Copyright 2012 Nature Publication Group

edges accessible in short path. Apart from structure control, doping chemistry is applied to extend active by incorporating Ni, Co, Fe in cationic site, and Se in anion site, respectively [160-163]. Among them, Co promoted MoS₂ backed up by DFT calculations achieves outstanding performance relative to Fe, Ni in a similar content, which is based on the fact that Co bonding to S-edge downshifts $\Delta G^\circ_{\text{H}}$ to further close to Pt, *i.e.* zero Gibbs free energy [161].

Amorphous molybdenum sulfides are another family of non-noble catalyst for HER. They are distinguished from edge-rich metallic/semi-metallic MoS₂, where the abundant edges are the active sites for hydrogen generation to occur. Effects on developing amorphous molybdenum sulfides includes thin film *via* electrochemical deposition [161, 164-166], particles wet-chemical synthesis [167-171]. It is proposed by Hu *et al.* that the unsaturated Mo and S are the active sites for HER [167], and this statement is based on the fact that post annealing that causes crystallization *e.g.* polycrystal at 350 °C and single crystal at 650 °C, would lead to degraded performance; the higher temperature the samples undergo, the lower activity they exhibit. Another

study by Benck *et al.* indicates that the amorphous molybdenum sulfide as the high active species for HER have the XPS profile resembling that of MoS₂ [168] after an activation process, which is consistent with the study by Hu *et al.*. Overall, for amorphous molybdenum sulfides, numbers of unsaturated Mo, S are responsible to catalyse HER as the S-edges do in crystal MoS₂. Here, molybdenum sulfide can be MoS₃, MoS₂, or MoS_{2+x} or in whichever it keeps amorphous state, in large electrochemical surface area, XPS patterns that resemble edges-rich MoS₂. Those attributes are set as the benchmarks for further development of amorphous molybdenum sulfide to advance the performance of non-noble catalyst for HER.

Regarding to earth-abundant elements based materials, *e.g.* molybdenum/tungsten sulfides, selenides, for photo-electrochemical/electro-chemical hydrogen generation, several reviews are conducted in different perspectives, and are directive conspectus in HER for future reference [172-177].

Carbides

One pronounced advantage of carbide materials, compared to molybdenum sulfide is their high conductivity. For example, tungsten carbides is reported to reach 10⁵ S/cm, and it is even comparable to metal [178]. Early investigation of carbides of group V metals (V, Nb Ta) and Ti, have shown poor catalytic activity towards HER [179-183]. Among all the carbide reported, tungsten carbide (WC, W₂C) and molybdenum carbide (Mo₂C, MoC) are the most promising candidates for the replacement of Pt, in term of cathodic hydrogen evolution and anodic fuel oxidation. But, the challenges are ensued in two aspects: (1) routinely, carbides are synthesized through carburization at high temperature using solid carbon or hydrocarbon as the carbon source. This facile, state-of-the-art route would lead to a surplus layer of carbon on the surface, which terminates the active site of carbides and hinders the subsequent Pt/Pd deposition; (2)

carbides are still lack of the competitive performance versus that of Pt, which more likely functions as effective support for Pt as is demonstrated in the case of methanol oxidation [184]. In Jinaguan G. Chen's group, efforts have been devoted to the removal of surface carbon [185-187], seeking for mon-layer noble metal (Pt/Pd) supported on WC [188], Mo₂C/W₂C [189]. The intention is to enhance the interaction between carbide and catalyst, *i.e.* Pt/Pd, and circumvent the poor catalytic activity of carbide by imposing additional mon-layered noble catalysts. However, to target the ultimate goal, *i.e.* in seek of non-noble, cost-effective catalysts, introduction of Pt/Pd should not be intentional. A report of Mo₂C by Hu *et al.* draw attention to development of carbide as an non-noble catalyst for HER [190]. It is found that electrolysis at a cathodic current would lead to activated Mo₂C that is able to achieve ~25 mA cm⁻² at an over-potential of 200 mV in acid. Besides, Mo₂C is also attested to be stable in alkaline, indicated by nearly sustained current density in 48 h. Sequential work demonstrates that there are still room for further improvement of the performance *via* fabrication in well-defined structure, *e.g.* Mo₂C/CNT [191, 192], integrated Mo₂C with rGO [193, 194], carbon [184, 195] as well as tungsten carbide [196]. The as-obtained high performance lies in the well-defined nano particles, evenly distributed on substrates *i.e.* CNT/graphene, which proliferates the surface of Mo₂C – active site for HER. The synergistic effect coupled with the substrates [191] can be another positive factor in the high activity towards HER. A more recent report of mesoporous Mo₂C strengthens the point that well-defined nano structure with high surface area would multiply the specific current density at fixed potential in orders of magnitude [197]. Our investigation of carbide as non-noble catalyst for HER is summarized in separate chapters. Overall, given the synthetic method, stability and activity of the catalyst among those carbides thereof, WC/W₂C, Mo₂C stand out with superior performance,

and are more of interest to researchers. More studies on tungsten/molybdenum carbides are to be continued.

Phosphides

Phosphides are typically used as the catalyst for hydrodesulfurization (HDS), *e.g.* Ni_2P [198, 199], MoP [200, 201]. Not until recently, phosphides are found to be very active towards HER. This is de facto due to a similar process that occurs on the catalyst – hydrogen species association/dissociation. Routinely, HDS reaction relies on adsorption of organosulfur and H_2 molecule on the catalyst followed by C–S cleavage and desorption of hydrocarbon fragments and formation of H_2S [201, 202]. This is analogous to reversed hydrogen production pathway where HER relies on the adsorption of proton and desorption of H_2 molecules [203].

Recently, reports of using HDS catalyst (phosphides) for HER burgeon, including FeP [204], Ni_2P [205], CoP [206], MoP [207] *etc.*. The study of Ni_2P for HER is firstly

Figure 1 - 11 Nanostructured Ni_2P particle for HER (A) LSV scan in 0.5 M H_2SO_4 ; (B) Tafel Plot of Ni_2P and Pt; (C) TEM image of as-synthesized Ni_2P nano particles. Reproduced with permission from Ref. [205]. Copyright (2013) American Chemical Society.

reported by Popczun *et al.* [205]. Figure 1-11A shows the polarization curves of Ni₂P where it achieves 20 mA cm⁻² and 100 mA cm⁻² at $\eta = 130$ mV and 180 mV respectively at a mass loading of 1 mg/cm² on 0.2 cm² Ti foil. More importantly, the onset potential is closer than ever to Pt, making it a promising candidate as the substitution for Pt. However, its stability is limited compared to Mo₂C aforementioned, which may possibly arise from morphological deterioration of the nanostructure in caustic media, *i.e.* 0.5 M H₂SO₄ & 1 M KOH, plus the chemical instability of Ni₂P in alkaline. On the other hand, the synthesis of Ni₂P involves use of tri-n-octylphosphine as the P source, and the whole experiment is conducted in organic phase. This sophisticated procedure may become a great barrier for practical use. The method for Ni₂P is applicable to CoP [206], MoP [208] and WP [209] by changing the transitional metal precursors, which were reported by the same group. Interestingly, catalyst synthesis *via* organic phosphine source results in crystal forms for Ni₂P and CoP, while amorphous forms for MoP and WP, but anyhow the as-obtained phosphides manifest a uniform morphology with well-define particles (less than 10 nm) and similar activities towards HER. It is noteworthy that annealing at high temperature should be avoided in this synthetic route (> 500 °C), especially for the amorphous MoP and WP, as high-temperature annealing would lead to severe sintering – formation of bulk phase, which only results in degraded performance.

Alternative to the organic synthetic route, we found that using ammonium molybdate tetra-hydrate ((NH₄)₆Mo₇O₂₄•4H₂O) and di-ammonium hydrophosphate ((NH₄)₂HPO₄) as the precursors, a facile reduction of the mixture thereof in hydrogen at high temperature (650 °C) makes highly active MoP, even in bulk phase [207, 210]. Comparative study of metal, Mo₃P and MoP reveals the importance of the degree of phosphorization, and theoretical calculation shows that P as the active site is

responsible for the high activity towards HER. The high performance is confirmed by other two reports [210, 211]. Besides, MoP is found to be a good catalyst in both acid and alkaline with high stability in 0.5 M H₂SO₄, showing its advantage over Ni₂P that is reported to be degrading rapidly in 1 M KOH [205], albeit a slight degradation is observed in 1 M KOH in 40 h.

Apart from the two method for the synthesis of phosphides aforementioned, Guan *et al.* reported a synthetic route by decomposing hypophosphite, which was adopted by Hu *et al.* [212] and Sun *et al.* [203, 213-218]. Benefiting from the controllable releasing of PH₃ that is used as P source as well as reductant, transitional metal compounds, *e.g.* Co₃O₄ [214], NiCl₂•6H₂O [212], Cu(OH)₂ [203] can be converted to their phosphides at relatively mild conditions (below 400 °C). Moreover, this mild condition for the synthesis of phosphides successfully preserves the morphology of its precursor, *i.e.* transitional metal compounds, the so-called ‘topotactic synthesis’ which stimulates a variety of reports of phosphides in different nanostructures, *e.g.* self-supported Cu₃P nano-wire from Cu(OH)₂ nano-wires, and CoP nano wire from Co₂(OH)₂(CO₃)₂ nano-wires [215] and FeP arrays from FeO(OH)₃ arrays [219] *etc.*. Overall, the as-obtained high performance is ascribed to the well-defined nanostructure that is consisted of nanoparticles assembly.

In a nutshell, phosphides as a newly recognized catalyst for HER exhibit advantageous performance over molybdenum sulfides, and this highlighted advantages lie in those features: (1) low onset potential, ~ 40 mV for CoP [214] *vs.* 150 ~ 200 mV for that of MoS₂ [148]; (2) transitional metal phosphides exhibit metallic properties, *i.e.*, high electrical conductivity [203, 220, 221], and this is indicated by the fact that higher mass loading (2 mg cm⁻² *vs.* 0.9 mg cm⁻²) leads to better performance [206], unlike

MoS₂, dominated by thin-layer configuration [155] due to its sluggish electron transfer among layers; (3) Phosphides are free from the constraint of fabrication of layered structure or nanostructure that guarantees the superb performance for MoS₂. Here, bulk MoP is found to be very active towards HER, and this feature enables facile synthesis of phosphides, making it more practical for industrial use. Challenges are co-existing. Revealed by XPS, surface oxidation occurs under ambient condition, in the formation of P (V) and Mo (V/VI) in the case of MoP. This as-formed high-valence state blocks the access of proton to the active site, which will result in poor performance. Future researches are warranted to advance a more stable, highly active non-noble catalyst for HER, *e.g.* phosphides or their derivatives.

Others

Non-noble catalysts are booming to date for catering the increasing demand of energy, and cost-effective catalyst are always desired, which drives the investigation of carbon based materials for HER. Recently, it is found that under a certain activation process, carbon materials are active towards HER. Studies including carbon nanotube [222, 223], C₃N₄ [224], doped graphene [225] are reported as metal-free catalyst. Besides, the performance are further enhanced by the incorporation of cobalt [226-228] or other metals in a hybrid [229], and in this hybrid, the improved performance is originated from the metals with protective carbon layers on top, so that it is able to catalyse HER stably in acid. However, neither metal-free carbonaceous catalyst nor cobalt embedded carbon materials meet the goal that is set for hydrogen production, nor can they supplant well developed sulfides, carbides, phosphides. Although activated carbon materials (including graphitic carbon, carbon nanotubes) are reported recently to have [230] achieved remarkably high performance that is close to Pt, insights into the active site are still needed, and further scientific evidences are called forth.

1.3 Objectives of the thesis

In this thesis, we peculiarly place our focus on hydrogen energy in two aspects – hydrogen oxidation and hydrogen production. Our selectively opt for molybdenum based materials is with the consideration that firstly, molybdenum as an earth-abundant element compared to Pt, would be cost-effective as a catalyst or starting material for catalyst; secondly, as a transition metal, molybdenum with tunable electron structure has formed a variety of compound, and some of them, *e.g.* carbides, phosphides, have exhibited intriguing activity as catalysts in fuel cells, HDS reaction *etc.*; thirdly, molybdenum compound are usually found to have high conductivity, which is one of the core values required for the application as either catalyst or substrate for catalyst. For example, MoO₂ is reported a conductivity of 400 S/cm [231].

For hydrogen oxidation, we rely on one model of fuel cells – solid oxide fuel cell, and aim for the advancement of perovskite material. The objective in this thesis for hydrogen oxidation on perovskite materials is to separate conductive and catalytic constituents into two individuals. With the optimal ratio of the two, we aim for both enhanced conductivity and catalytic activity at SOFC's work condition (800 °C), *via* wet-chemical infiltration and doping techniques.

For hydrogen production, we aim for the development of non-noble catalyst as potential substitutes for Pt in both acid and alkaline. Based on those molybdenum compounds that are used in fuel cells/HDS reaction, we make our investigations on the catalysts of their catalytic activity, electrical conductivity, resistivity to the corrosion in acid and alkaline. Concerning the core property for a catalyst – the catalytic activity, we seek new synthetic routes for the preparation of nanostructured molybdenum compounds, and pursue new non-noble catalysts for HER. Through analysis of the

results that are collected from the electrochemical tests, structural engineering, and surface properties probed by XPS *etc.*, we made a comparative study of the non-noble molybdenum compounds with Pt. Perspectives are given to further push the realization of economic and reliable hydrogen energy in future.

Chapter 2 H₂ and CH₄ oxidation on Gd_{0.2}Ce_{0.8}O_{1.9} infiltrated SrMoO₃-yttria-stabilized zirconia anode for solid oxide fuel cells

(This chapter is reproduced with the permission from P. Xiao, X. Ge, L. Zhang, et al., *H₂ and CH₄ oxidation on Gd_{0.2}Ce_{0.8}O_{1.9} infiltrated SrMoO₃-yttria-stabilized zirconia anode for solid oxide fuel cells*. International Journal of Hydrogen Energy, 2012. 37(23): p. 18349-18356. Copyright 2012 Hydrogen Energy Publications)

2.1. Introduction

Solid oxide fuel cells (SOFCs) are promising energy conversion devices due to its high conversion efficiency and fuel flexibility, ranging from hydrogen, biogas, to pure hydrocarbons. The state-of-the-art Ni based anodes, such as Ni/8Y₂O₃-ZrO₂ (Ni-YSZ), work satisfactorily with H₂ because of the high electrochemical catalytic activity of Ni. Unfortunately, Ni-YSZ anode suffers from severe carbon deposition and subsequent loss of active sites when hydrocarbons such as methane are used as fuels [51, 232]. Adding H₂O to reform hydrocarbons has been demonstrated to be an effective way to mitigate the coking problem. However, high content of H₂O deteriorates the cell and increases the complexity of SOFC systems [50]. Alternatively, the development of a nickel-free anode material with competitive conductivity and electro-catalytic activity to Ni-YSZ has been pursued by many researchers. Among these efforts, perovskite materials, such as (La_{0.75}Sr_{0.25})_{0.95}Cr_{0.5}Mn_{0.5}O_{3-σ} (LSCM) [92, 233] and Sr₂MMoO₆ (M=Mn, Mg) [57], achieved high performance. Recently, SrMoO₃ [1] attracts our attention due to its high conductivity in the order of magnitude of 10³ S cm⁻¹ at a temperature of 727 °C. A SrMoO₃-infiltrated YSZ anode exhibits high conductivity of 20 S cm⁻¹, which satisfies the electrical conductivity requirement for the anode [234, 235] but suffers from very low electro-catalytic activity. Considering the difficulty to adopt a single oxide material to fulfil both high conductivity and catalytic activity

simultaneously, the incorporation of two separate materials appears practical for the tuning of these two properties independently. It is well known that CeO₂ or Gd doped CeO₂ (Gd_{0.2}Ce_{0.8}O_{1.9}, GDC) has good catalytic property towards fuel oxidation. For example, Gross et al.[94] reported that, with 40 wt.% CeO₂ loading on Pd-YSZ, the maximum power density ($P_{\max}$) increased to 520 mW cm⁻², compared to 360 mW cm⁻² with 20 wt.% CeO₂ loading on Pd-YSZ in wet H₂ at 700 °C. GDC-impregnated La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O₃ (LSCM) was also reported to have high activity towards direct CH₄ oxidation [236]. In the case of nano-coated GDC on Ni, enhanced redox cycling stability was observed for CH₄ oxidation [237].

In the present study, a Ni-free anode was fabricated by GDC impregnation onto SrMoO₃-YSZ scaffold in electrolyte-supported cells. The effects of SrMoO₃ on the electrode conductivity and GDC on the catalytic activity were respectively examined. Salient performance is achieved under wet H₂ in the temperature range from 800 °C to 900 °C. With GDC loading of 2.8 mg cm⁻², the polarization resistance (R_p) for H₂ oxidation decreases to 0.5 Ω cm², compared to nearly no activities of SrMoO₃-YSZ anodes.

2.2. Experimental

SrMoO₄ powders were prepared by solid state reaction of ball milled SrCO₃ (Sigma-Aldrich) and, MoO₃ (Sigma-Aldrich), in iso-propanol for 24 h, followed by calcination in air for 10 h at 1200 °C. The as-synthesized SrMoO₄ powder was mixed with YSZ in different ratios (in 90 wt.%, 70 wt.%, 50 wt.% of SrMoO₄) in a mortar. The mixture was then dispersed in iso-propanol and ball-milled for 24 h. After drying, the SrMoO₄-YSZ composites were made into an anode paste with ink vehicle (VEH, Fuel Cell Material) and SrMoO₃-YSZ anodes were obtained by reducing SrMoO₄-YSZ under H₂. An electrolyte-supported cell was used in this study. 8mol% yttria-stabilized zirconia

(YSZ) (YSZ, Tosoh, Japan) powders were die pressed into pellets and sintered, at 1500 °C for 4 h. The as-prepared YSZ substrates were 19 mm in diameter and 1 mm in thickness. The anode paste was subsequently painted onto a YSZ electrolyte disk and then sintered at 1300 °C in air for 2 h to form a thin anode layer (~30 µm) with an active area of 0.5 cm². Gd_{0.2}Ce_{0.8}O_{1.9} was introduced into the anode layer by wet impregnation of 1M stoichiometric Gd(NO₃)₃ (Sigma-Aldrich) and Ce(NO₃)₃ (Sigma-Aldrich) aqueous solution. Then, it was placed in the vacuum oven at 100 °C to facilitate the infiltration process. After that, the anode was sintered at 900 °C for 1 h to form a yellowish GDC phase. Different loadings of GDC were achieved by repeating the aforementioned process several times. Then, a small amount of Pt paste was painted in the center of the anode surface as a current collector to ensure good contact between the anode and the Pt mesh. Au wires were applied to ensure the electrical connection outside the furnace.

Half-cell electrochemical tests were conducted in a three-electrode configuration, similar to the one described elsewhere [238]. Briefly, Pt paste was painted as the counter electrode on the opposite side of the anode with the same area and the reference electrode was painted on the side of the counter electrode in two arc bars. The distance between the reference electrodes and counter electrode was 5 mm. Finally, the half cells were mounted against an alumina tube and sealed by ceramic adhesive (Ceramabond 552, Aremco). Wet CH₄ oxidation and redox cycling stability test under wet H₂ were conducted in a single cell by applying 300 µm YSZ pellet (Fuel Cell Material) as the electrolyte substrate, La_{0.8}Sr_{0.2}MnO_{3-δ} (LSM, Fuel Cell Material) mixed 40 wt.% YSZ as the cathode and GDC infiltrated SrMoO₃ (50 wt.%)/YSZ as the anode. For all the electrochemical tests, dry or wet H₂ and CH₄ (~3% H₂O, bubbling from a water tank at room temperature) was fed as fuel to the anode at a flow

rate of 50 sccm controlled by a mass flow controller (Cole-Parmer), and the cathode was exposed to ambient air. Electrochemical Impedances Spectroscopy (EIS) was carried out using VersaSTAT-3F (Princeton Applied Research) in potentiostatic mode from 100 kHz to 0.1 Hz or 0.01 Hz under open circuit voltage (OCV) conditions with ac amplitude of 20 mV. Selected EIS data were fitted by Zview program. The microstructure was examined by field-emission scanning electron microscopy (FE-SEM, JOEL, JSM6701, Japan), and the phase structure of the as-synthesized $SrMoO_4$ and GDC crystalline phase were characterized by X-ray diffraction (XRD), from Cu $K\alpha$ radiation source (Bruker, Japan).

2.3. Results and discussion

2.3.1. Characterization of $SrMoO_3$ -YSZ anode in H_2 oxidation

Figure 2-1a shows the XRD pattern of the as-synthesized $SrMoO_4$ powder. Characteristic peaks are identical to $SrMoO_4$ pattern in Figure 2-1b (PDF 00-008-0042) and no major second phase is observed. The $SrMoO_4$ -YSZ electrode was reduced to $SrMoO_3$ -YSZ by in-situ exposure to wet H_2 (~ 3% H_2O) at 900 °C for 2 h. Figure 2-1e and Figure 2-1d show the XRD comparison between these two samples. Despite 2 h reduction, the $SrMoO_4$ phase can still be observed, which indicates that $SrMoO_4$ is difficult to be reduced completely even under SOFC operation condition. This agrees with what Baldychev *et al.* [239] have observed. As shown in Figure 2-1c, no other components are detected in GDC-infiltrated anodes. To balance the electronic conductivity and oxygen ionic conductivity, $SrMoO_3$ -YSZ anodes of different weight ratios were prepared. Impedance measurements were subsequently conducted at 800 °C under wet H_2 atmosphere. As shown in Figure 2-2, Ohmic resistance (R_Ω , determined from the high frequency intercept) almost remains unchanged when the content of $SrMoO_3$ is higher than 50 wt.%.

Figure 2 - 1 XRD patterns (a) synthesized $SrMoO_4$; (b) standard $SrMoO_4$ PDF card; (c) GDC infiltrated $SrMoO_3$ -YSZ; (d) $SrMoO_3$ -YSZ anode; (e) $SrMoO_4$ -YSZ.

Only when the $SrMoO_3$ -YSZ ratio was decreased to 3:7, a dramatic increase of R_Ω to $4 \Omega \text{ cm}^2$ occurred, implying that high YSZ content may block the electron pathways through the anode. $SrMoO_3$ (50 wt.)/YSZ has the lowest R_p of $8 \Omega \text{ cm}^2$ (determined from the difference between the low frequency and high frequency intercepts) for wet H_2 oxidation at 800°C , compared to $19 \Omega \text{ cm}^2$ and $16 \Omega \text{ cm}^2$ for $SrMoO_3$ (90 wt.)/YSZ and $SrMoO_3$ (70 wt.)/YSZ respectively.

Figure 2 - 2 Impedance spectra for H₂ oxidation at 800 °C on SrMoO₃-YSZ anodes with different weight ratio.

The effect of SrMoO₃-YSZ ratio on the electrode morphology was examined by SEM in Figure 2-3. Severe sintering occurs on the SrMoO₃ (90 wt.%)/YSZ and SrMoO₃ (70 wt.%)/YSZ.

Figure 2 - 3 surface morphology for different SrMoO₃-YSZ anodes: (a) SrMoO₃ (90 wt.%)/YSZ; (b) SrMoO₃ (70 wt.%)/YSZ; (c) SrMoO₃ (50 wt.%)/YSZ; (d) GDC infiltrated SrMoO₃ (50 wt.%)/YSZ.

Particularly for $SrMoO_3$ (90 wt.%)/YSZ, the particles agglomerate to several micrometers, resulting in a decreased catalytically active interface. This may explain the surprisingly large R_p of this electrode. However, when the YSZ content was increased to 50 wt.% (Figure 2-3c), there is much less agglomeration and the necks between $SrMoO_3$ -YSZ particles could be clearly observed. One possible reason is that strontium molybdate is easier to sinter than YSZ. To some degree, the presence of more YSZ can mitigate particle agglomeration. A similar phenomenon was observed in a previous report by Jiang et al. [240].

2.3.2. Effect of GDC infiltration on H_2 oxidation

GDC was introduced into the $SrMoO_3$ -YSZ anode by wet impregnation.

Figure 2 - 4 Impedance spectra at 800 °C on $SrMoO_3$ (50 wt.%)/YSZ (diamond), 14 wt.% GDC infiltrated $SrMoO_3$ (50 wt.%)/YSZ (rectangle), 56 wt.% GDC infiltrated $SrMoO_3$ (50 wt.%)/YSZ (circle) in $H_2/3\% H_2O$ and their fitted results using an equivalent circuit shown below

As shown in Figure 2-3d, GDC nanoparticles with size ranging from 50 nm to 100 nm evenly spread on the $SrMoO_3$ -YSZ scaffold, especially on the sintering necks among different particles, leads to extended active reaction sites. According to the mixed ionic and electronic conductivity (MIEC) [241, 242] due to Gd doping and Ce^{4+} reduction, infiltrated GDC nano-particles covering the YSZ or $SrMoO_3$ may create new pathways for electrons and oxide ions in the anode, which could enhance the electrochemical activity. Figure 2-4 shows the impedance spectra after the subtraction of the R_Ω of 1 mm YSZ electrolyte, which were measured at 800 °C for half cells under OCV condition. Without GDC infiltration, R_p for H_2 oxidation is $8 \Omega \text{ cm}^2$. When 0.7 mg cm^{-2} GDC was incorporated, R_p decreased to $2.2 \Omega \text{ cm}^2$. It further dropped to $0.5 \Omega \text{ cm}^2$ when GDC infiltration loading was increased to 2.8 mg cm^{-2} . These results illustrate that nano-sized Gd doped ceria particles can greatly improve the performance for H_2 oxidation. Similar performance enhancement was also obtained by doped ceria [123, 243].

H_2 oxidation in SOFCs generally involves charge transfer process and mass transport process [244, 245]. An equivalent circuit $L_1(R_1 \text{ CPE}_1)(R_2 \text{ CPE}_2)$ was used to fit the EIS data via the Zview program and the fitted result is shown in the inset of Figure 2-4. The inductance L_1 is caused by the Au wires. The high frequency resistance R_1 which corresponds to the charge transfer process, decreases from $0.32 \Omega \text{ cm}^2$ to $0.10 \Omega \text{ cm}^2$ when the GDC loading is increasing from 0.7 mg cm^{-2} to 2.8 mg cm^{-2} . In the meantime, low frequency resistance R_2 which represents the mass transport process and includes the bulk gas diffusion, oxide ions transport and the dissociative adsorption of molecular species to triple phase boundaries (TPB) [245, 246], decreases from $1.88 \Omega \text{ cm}^2$ to $0.44 \Omega \text{ cm}^2$. Among them, the gas diffusion of H_2 and its dissociative adsorption process are not rate-dominating processes. Possibly, oxide ions

transportation contributes to the large arc in EIS, which indicates it is still the rate-determining process. But, the fitted results show that both processes are promoted by GDC infiltration.

Figure 2-5 displays the overpotential for H_2 oxidation on half cells, which could directly reflect the kinetic behavior of anodes. In contrast to bare $SrMoO_3$ (50 wt.%)/YSZ, the overpotential for GDC infiltrated anodes decreases sharply, especially at high current densities. For instance, the overpotential for 2.8 mg cm^{-2} GDC infiltrated anode is only 0.14V when drawing a current density $0.8 A cm^{-2}$, which is comparable to GDC- $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$ (LSCM), [236] $\sim 0.1V$ when $0.6 A cm^{-2}$ is applied.

Figure 2 - 5 Overpotential for different amount of GDC loading on $SrMoO_3$ (50 wt.%)/YSZ anode at 800 °C in $H_2/3\% H_2O$

2.3.3 Redox cycling stability test for GDC infiltrated $SrMoO_3$ -YSZ anode

Redox cycling stability is critical for long term operation of SOFCs. It is known that the state-of-the-art Ni based cermet anode, such as Ni-YSZ, possesses low redox cycling stability. Ni oxidation could cause up to 69.2% volume expansion [56], which is more severe than 28 % volume change upon the reduction of $SrMoO_4$ to

$SrMoO_3$ [247]. Sr-doped $CeVO_3$ [248] and Ca-doped $CeVO_3$ [249] have different redox reversibility for different amount of doping. In this study, redox cycling stability of the GDC infiltrated $SrMoO_3$ -YSZ anode was examined at 900 °C on a single cell under wet H_2 . After reduction, N_2 was applied to purge H_2 , followed by air oxidation. I-V-P curves and impedance spectra were then recorded (Figure 2-6). After 5 redox cycles, the maximum power output drops slightly from 342 $mW\ cm^{-2}$ to 320 $mW\ cm^{-2}$ (Figure 2-6a), corresponding to a slight increase on the impedance spectra in Fig. 6b, accordingly.

Figure 2 - 6 Redox stability test at 900 °C on single cell GDC, $SrMoO_3$ -YSZ|YSZ|LSM-YSZ, (a) I-V-P curves; (b) impedance spectra under open circuit voltage.

Figure 2-7a shows some broken lines along the anode/electrolyte interface. This is in

contrast to the freshly prepared cell (Figure 2-7b) where good adhesion between the anode and electrolyte is evident. These broken lines can be explained by the volume

Figure 2 - 7 Cross section view (a) fresh cell; (b) after 5 redox cycles test;

fluctuation of $SrMoO_3$ and GDC during redox cycling. Among the anode components, YSZ is very stable and little structure or lattice volume change occurs upon redox cycling. In contrast, doped ceria will be reduced under anodic operation condition, forming Ce^{4+}/Ce^{3+} couple thus incurring phase transformation upon redox cycling. Besides, phase transition from tetragonal scheelite to cubic perovskite leads to 28 vol.% decrease when $SrMoO_4$ is reduced to $SrMoO_3$, even though no delamination was observed after the test under macroscopic observation.

2.3.4 Influence of water content on cell performance in H_2 oxidation

The observation of $SrMoO_4$ as a minor phase from XRD analysis necessitates the investigation of water effect on the $SrMoO_3/SrMoO_4$ redox couple and cell performance. Figure 2-8 presents the power output and impedance spectra of anode exposed to dry and wet H_2 . Clearly, dry H_2 provides higher performance (426 mW cm^{-2} vs 342 mW cm^{-2}) and higher OCV (1.13V vs 1.05V) than wet H_2 . Impedance spectra (Figure 2-8b) show that the R_{Ω} decreases from $0.56 \Omega \text{ cm}^2$ to $0.41 \Omega \text{ cm}^2$ when switching to dry H_2 . By referring to the literature [250, 251] for the ion conductivity of YSZ, the 300μm YSZ pellet contributes $0.36 \Omega \text{ cm}^2$ at 900 °C. By comparison, the

presence of 3% H_2O could incur the oxidation of conductive $SrMoO_3$ to insulating $SrMoO_4$, rendering the increase of R_Ω for GDC infiltrated $SrMoO_3$ -YSZ anode. Lower partial pressure of hydrogen may also be less efficient in reducing $SrMoO_4$ to $SrMoO_3$. On the other hand, likewise the water to Ni-YSZ anode [252], 3% H_2O can decrease the polarization resistance from $0.5 \Omega \text{ cm}^2$ to $0.25 \Omega \text{ cm}^2$ in this study. Probably it is the pre-absorbed water or its decomposed hydroxyl species on TPB that accelerates the process of H_2 oxidation [253]. Considering this, further experiments on $SrMoO_3$ -YSZ

Figure 2 - 8 (a) I-V-P curve for dry and wet H_2 oxidation at 900 °C and (b) their EIS curves, respectively under OCV condition.

anode are needed to probe the optimum operation conditions in order to achieve a better performance.

2.4. Conclusions

The properties of strontium molybdate as an electronic conductor incorporated with YSZ were examined. Because of limited catalysis of SrMoO₃-YSZ towards H₂ and CH₄ oxidation, GDC was infiltrated into the SrMoO₃-YSZ scaffold through wet impregnation. Electrochemical characterization showed that cell performance was greatly improved by the incorporation of GDC, both in H₂ and CH₄. The R_p decreased from 8 to 0.5 $\Omega \text{ cm}^2$ at 800 °C for wet H₂ oxidation, which is comparable to the previously reported SrMoO₃ infiltrated on YSZ scaffold with additional Pd loading. Without additional loading of Pd [1], OCV for wet CH₄ is much lower than the theoretical value, only 873mV at 850 °C, possibly due to the low activity of GDC towards CH₄ cracking. As a potential anode for hydrocarbon utilization, the GDC infiltrated SrMoO₃-YSZ showed no carbon deposition problem and achieved a P_{max} of 160 mW cm⁻² when exposed to wet CH₄ at 900 °C. While the single cell performance slightly decreased after 5 redox cycles, no fatal delamination was observed. Investigation of the influence of H₂O suggests SrMoO₃ is sensitive to the operation conditions and the presence of 3% H₂O leads to the increase of R_Ω but decrease of R_p .

Chapter 3 Sr_{1-x}Ca_xMoO₃–Gd_{0.2}Ce_{0.8}O_{1.9} as the anode in solid oxide fuel cells: effects of Mo precipitation

(This chapter is reproduced with permission from P. Xiao, X. Ge, Z. Liu, et al., *Sr_{1-x}Ca_xMoO₃–Gd_{0.2}Ce_{0.8}O_{1.9} as the anode in solid oxide fuel cells: Effects of Mo precipitation*. Journal of Alloys and Compounds, 2014. **587**(0): p. 326-33. Copyright 2014, Elsevier)

3.1. Introduction

Solid oxide fuel cells (SOFCs) are highly efficient power generators for direct conversion of chemical energy to electrical energy. The state-of-the-art Ni–YSZ anode has achieved high performance towards H₂ oxidation at high temperature due to the high catalytic activity of Ni, but unfortunately its negative attributes are also disclosed, *e.g.* low tolerance to hydrocarbons and hydrogen sulfide, poor redox stability [50, 51, 254, 255]. The development of nickel-free anode with competitive conductivity and electro-catalytic activity to Ni–YSZ has been pursued by many researchers [234, 235, 256, 257]. Among them, (La_{0.75}Sr_{0.25})_{0.95}Cr_{0.5}Mn_{0.5}O_{3-σ} (LSCM) [92, 233], Sr₂MMoO₆ (M=Mn, Mg) [57] and Sr₂Fe_{1.5}Mo_{0.5}O_{6-σ} [111] achieved high redox stability and resistivity towards hydrocarbons and hydrogen sulfide, but with the compromise of power density especially at intermediate temperature (600 °C ~ 800 °C). Although increased performance could be achieved by wet impregnation of 2 wt.% Ni [258], Pd/CeO₂ [259], the agglomeration of the nanoparticles might happen under long-term operation. It has been proposed that durability can be improved if those impregnated nanoparticles can possess the ability of solving in and exsolving out of its host. Self-regenerative M (M=Pd, Pt, Rh, Ru) on perovskite or lanthanum chromite materials were first adopted in automotive emission control and methane reforming [260-263]. In-situ segregated metal nanoparticles on ceramic materials that react generatively can be a potential solution to the poor catalytic activity of ceramic anode materials towards

H₂ and hydrocarbons oxidation. Successful cases [264-267] have been reported to tailor the properties of materials by doping other elements. A Ru doped lanthanum chromite based ceramic by Barnett *et al.* [102, 268, 269] demonstrated an improved performance due to Ru cluster segregation. Yang *et al.* [270] also reported a redox reversible anode composed of Pr_{0.8}Sr_{1.2}(Co, Fe)_{0.8}Nb_{0.2}O_{4+δ} (K-PSCFN), which can be obtained by reducing perovskite structure material Pr_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.7}Nb_{0.1}O₃ (P-PSCFN) in H₂. Regenerative behaviour was observed and high performance was achieved towards both H₂ and CH₄ oxidation due to the segregated Co-Fe alloy. Recently, a highly conductive ceramic material SrMoO₃ has been reported to be a potential candidate to replace Ni [271, 272]. But further work [1] showed a rather low activity towards CH₄ oxidation without additional Pd infiltration. Considering the difficulty for a sole oxide material to perform as well as Ni cermet, GDC (Ce_{0.8}Gd_{0.2}O_{3-δ}) as a mixed ionic and electronic conductor (MIEC) [273, 274] was infiltrated on SrMoO₃–YSZ compound as the anode for SOFCs in our previous work [275]. Although improved performance has been observed, its application was hindered by its limited catalytic activity at the intermediate temperature range (600 ~ 800 °C).

Herein, we report an anode composed of Ca substituted strontium molybdate Sr_{1-x}Ca_xMoO₃ (x=0.3, 0.5) and GDC for SOFCs. As a potential anode, its performance was investigated in H₂. By introducing Ca on the A site, it is found for the first time that, Mo nanoparticles can reversibly segregate on the surface of Sr_{1-x}Ca_xMoO₃–GDC and perform as the catalyst. In this study, we analysed the effect of the Mo precipitation and further compared the electrochemical performance of Sr_{1-x}Ca_xMoO₃ with SrMoO₃.

3.2. Experimental

3.2.1. Materials synthesis

Sr(NO₃)₂ (ACS reagent, ≥99%), Ca(NO₃)₂•4H₂O (ACS reagent, ≥99%) and (NH₄)₆Mo₇O₂₄•4H₂O (BioUltra, ≥99.0%, Sigma-Aldrich) are used as received from Sigma-Aldrich. Gadolinium doped ceria (GDC, Gd 20 mol.%, TC grade) was purchase from Fuel Cell Materials.

Sr_{1-x}Ca_xMoO₄ (x=0, 0.3, 0.5, SCMO_{ox}) were synthesized via a sol-gel method assisted by citric acid [276, 277] as the chelate reagent. Calculated stoichiometric Sr(NO₃)₂, Ca(NO₃)₂•4H₂O and (NH₄)₆Mo₇O₂₄•4H₂O were mixed with citric acid with the molar ratio of 1:1.5 (metal ion to citric acid) in distilled water at 90 °C under continuous stirring. After slow evaporation of water, a yellowish gel was formed, which was transferred to an oven for ignition treatment at 300 °C for 2 h. The as-obtained powder was ground in a mortar and then pressed into pellets, sintered at 800 °C for 10 h to form crystalline phase in the formula of Sr_{1-x}Ca_xMoO₄ (SCMO_{ox}). The SCMO_{ox} powder can be obtained by mild grinding the sintered pellets. Sr_{1-x}Ca_xMoO₃ (SCMO_{re}) was finally synthesized by a further reduction of SCMO_{ox} in pure H₂ at 900 °C.

3.2.2 Materials characterization

The phase structure of the as-synthesized powder was examined by X-ray diffraction using Cu Kα radiation source (Bruker, Japan). The morphology of the anode was examined on field emission scanning electron microscope (FE-SEM, JEOL, JSM6701F, Japan). Thermo-gravimetric analysis (TGA) coupled with differential scanning calorimetry (DSC) of Sr_{1-x}Ca_xMoO₃ (x=0, 0.3, 0.5, SCMO_{re}) were conducted at a ramping temperature 15 °C/min (TGA, Perkin Elmer) in air.

3.2.3 Fuel cell test

The Sr_{1-x}Ca_xMoO₄–GDC composite was prepared by dispersing Sr_{1-x}Ca_xMoO₄ and GDC into iso-propanol, which was then ball-milled for 24 h and dried. Anode paste

was prepared by mixing $Sr_{1-x}Ca_xMoO_4$ -GDC composite with the ink vehicle (VEH, Fuel Cell Materials). A $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$ (LSGM) electrolyte supported cell was used in the study. LSGM powder (Fuel Cell Material, USA) was firstly die pressed into pellets and then sintered at 1450 °C for 5 h. The obtained LSGM disks were polished into thin electrolytes of ~350 µm thickness. Anode pasted was painted onto the electrolyte and subsequently sintered at 1150 °C for 2 h with an active area of 0.28 cm². $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF, Sigma-Aldrich) was used as cathode. To circumvent the possible catalytic activity introduced by Pt paste, Ag paste was used as the current collector for anode. $Sr_{1-x}Ca_xMoO_3$ -GDC ($SCMO_{re}$ -GDC) anodes were finally obtained by in-situ H₂ reduction. After stabilization in H₂ for 2 h, subsequent electrochemical measurements were implemented.

A typical home-made alumina tube was used for single cell test. Fuel cell tests were conducted at 800 °C under atmospheric pressure, with H₂ or CH₄ fed at the rate of 50 sccm in the anode whilst the cathode was exposed to ambient air. Current-voltage-power (I-V-P) curves were recorded by a VersaSTAT-3F (Princeton Applied Research). Electrochemical impedance spectroscopy (EIS) was carried out under open circuit voltage (OCV) in a potentiostatic mode from 100 kHz to 0.1 Hz with an AC amplitude of 10 mV.

3.3. Results and discussion

3.3.1 Metal Mo segregation on $Sr_{1-x}Ca_xMoO_3$ and the structure analysis

Figure 3-1 shows the XRD pattern of $Sr_{1-x}Ca_xMoO_4$ (x=0, 0.3, 0.5). A typical tetragonal Scheelite structure of $SrMoO_4$ was indexed (JCPDS 08-0482), which implies that $SCMO_{ox}$ can be successfully synthesized at 800 °C for 10 h. However, XRD pattern still displays a minor peak at 25.05°, which can be assigned to (111) plane of strontium carbonate. This is possibly caused by a slight adsorption of CO₂

during sintering, and similar phenomenon was observed for $SrTiO_3$ synthesis [278]. Upon reduction treatment at 900 °C in H_2 during the synthesis of $SCMO_{re}$, this impurity phase can be completely eliminated, as confirmed by XRD in Fig. 2. In

Figure 3 - 1 XRD pattern of (a) $SrMoO_4$; (b) $Sr_{0.7}Ca_{0.3}MoO_4$; (c) $Sr_{0.5}Ca_{0.5}MoO_4$.

contrast to Figure 3-1a, Figure 3-1b and 3-1c show that the peaks, *e.g.* the (112) peak, gradually shift to higher angle, which implies the successful calcium dissolution into lattice for the 30 mol.% and 50 mol.% substituted strontium molybdate. Besides, as shown in Figure 3-1c, the high content of calcium incorporated into the A site leads to the peak splitting and broadening, possibly caused by the lattice distortion due to the ionic radius aberration, Sr^{2+} (1.44 Å) [113] *vs.* Ca^{2+} (1.34 Å) [279]. After reduction, $SCMO_{re}$ exhibits a perovskite structure in Figure 3-2. With the introduction of Ca into A site, we can also observe a gradual peak shift towards higher angle from $SrMoO_3$ to $Sr_{0.5}Ca_{0.5}MoO_3$, which corresponds to the decreased d-spacing. This evidenced the

retention of Ca in the lattice under reducing condition, instead of existing in a secondary phase. Furthermore, when Ca partially replaces Sr on A site to form

Figure 3 - 2 XRD patterns of (a) $SrMoO_3$; (b) $Sr_{0.7}Ca_{0.3}MoO_3$; (c) $Sr_{0.5}Ca_{0.5}MoO_3$.

$Sr_{0.7}Ca_{0.3}MoO_3$ and $Sr_{0.5}Ca_{0.5}MoO_3$, a new peak can be indexed at 40.5° in Figure 3-2, which corresponds to (110) of metallic Mo (JCPDS 42-1120). Mo precipitation is not outstanding when 30 mol.% Ca substitutes for Sr, while the presence of Mo is significant when the Ca content was further increased to 50 mol.%. The structure analysis by the Rietveld Method was carried out using TOPAS. The experimental and calculated profiles of X-ray diffraction data are presented in Figure. 3-3 and their refinement parameters are listed in Table 3-1. The profile refinements converge to a good solution in space group Pm3m (221), Pm3m (221) and I4/mcm (140) for $SrMoO_3$, $Sr_{0.7}Ca_{0.3}MoO_3$ and $Sr_{0.5}Ca_{0.5}MoO_3$ respectively. With increasing content of Ca, the structure transits from cubic to tetragonal perovskite. From the graphs presented in Figure 3-4c and 3-4d, we can clearly see that the MoO_6 octahedrons tilt along z axis(c direction) when 50 mol.% Ca is substituted for Sr on the A site, which is in contrast to cubic $SrMoO_3$ and $Sr_{0.7}Ca_{0.3}MoO_3$ (Figure 3-4a and 3-4b). This tilting is obviously caused by Ca (1.34 Å) replacement of Sr (1.44 Å).

Figure 3 - 3 Rietveld Method on (a) SrMoO_3 ; (b) $\text{Sr}_{0.7}\text{Ca}_{0.3}\text{MoO}_3$; (c) $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_3$.

Figure 3 - 4 Structure visualization of (a) and (b) for SrMoO_3 and $\text{Sr}_{0.7}\text{Ca}_{0.3}\text{MoO}_3$ (in cubic $\text{Pm}\bar{3}\text{m}$); (c) and (d) for $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_3$ (in tetragonal $I4/\text{mcm}$) ((c) and (d) are in view of c direction).

Table 3 - 1 Refinement results and crystallographic data for SrMoO_3 , $\text{Sr}_{0.7}\text{Ca}_{0.3}\text{MoO}_3$ and $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_3$ at room temperature

Nominal composition	SrMoO_3	$\text{Sr}_{0.7}\text{Ca}_{0.3}\text{MoO}_3$	$\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_3$
Space group	$\text{Pm}\bar{3}\text{m}(221)$	$\text{Pm}\bar{3}\text{m}(221)$	$I4/\text{mcm}(140)$
a (Å)	3.9752	3.9579	5.5757
c (Å)	–	–	7.8817
V (Å ³)	62.8174	62.0028	245.030
$\text{Sr}(\text{Ca})\text{--O}(1) \times 12\text{Å}$	2.8108	2.7987	2.5289
$\text{Sr}(\text{Ca})\text{--O}(2) \times 12\text{Å}$	–	–	2.7878
$\text{Mo--O}(1) \times 6\text{Å}$	1.9876	1.9789	1.9705
$\text{Mo--O}(2) \times 6\text{Å}$	–	–	2.0088
R_{wp} (%)	7.59	4.67	5.18
R_{p} (%)	5.57	3.37	3.66
χ^2	2.39	3.20	3.48

Previous analysis of Ru ex-solution and nucleation on lanthanum chromite were focused on the Ru diffusion in reducing condition by tracking the changes of the

particle size in the course of time [269]. Later, a DFT study on the regenerative behaviour of $LaFe_{1-x}M_xO_{3-y}$ ($M = Pd, Rh, Pt$) suggested the significance of oxygen vacancies (Vo) in favor of surface segregation [102, 280]. In our case, metal Mo precipitation could be detected by ex-situ characterization, *e.g.* SEM after reduction in H_2 in less than 2 h. As shown in Figure 3-5a and 3-5b, we can see the ex-solved Mo nucleates into several tens of nano-meters on the scaffold of $SCMO_{re}$ -GDC for both

Figure 3 - 5 Morphological graph by FESEM: (a) $Sr_{0.5}Ca_{0.5}MoO_3$ -GDC; (b) $Sr_{0.7}Ca_{0.3}MoO_3$ -GDC; (c) $Sr_{0.5}Ca_{0.5}MoO_4$ -GDC; (d) SEM image for cross-section view of a single cell

30 mol.% and 50 mol.% Ca-substituted strontium molybdate, which is in contrast to $SCMO_{ox}$ -GDC anode before reduction (Figure 3-5c). Considering the calculated bond length of Mo-O where Mo-O(1) of 1.9705 Å is shorter than 2.0088 Å of Mo-O(2) along the c direction, this lattice distortion could lead to structural instability. At high temperature in H_2 , $SCMO_{re}$ is not thermodynamic stable compared to the undoped one, which could possibly explain the Mo segregation on the surface.

3.3.2 Reversibility examination of Mo ex-solution

The segregated Mo nanoparticles tend to aggregate at high temperature. A regenerative anode would be a potential solution to the gradual performance degradation caused by particle agglomeration. To examine the reversibility of Mo segregation, XRD was carried out on $SCMO_{re}$ and $SCMO_{ox}$ powder after alternating treatment in H_2 and air.

Figure 3 - 6 XRD patterns of (a) fresh prepared $Sr_{0.5}Ca_{0.5}MoO_4$; (b) $Sr_{0.5}Ca_{0.5}MoO_3$ obtained by reducing fresh prepared $Sr_{0.5}Ca_{0.5}MoO_4$; (c) $Sr_{0.5}Ca_{0.5}MoO_3$ obtained after a redox cycle (the cycle to oxidize $Sr_{0.5}Ca_{0.5}MoO_3$ to $Sr_{0.5}Ca_{0.5}MoO_4$ and then reduce back)

Figure 3-6a exhibits the characteristic peaks of the fresh prepared $Sr_{0.5}Ca_{0.5}MoO_4$. Subsequent reduction of the fresh prepared $Sr_{0.5}Ca_{0.5}MoO_4$ in H_2 leads to the emergence of Mo (110) peak at 40.5° (Figure 3-6b). After another oxidation/reduction cycle, $Sr_{0.5}Ca_{0.5}MoO_3$ still retains its perovskite structure as shown in Figure 3-6c, which indicates the reversible behaviour of Mo segregation in response to reducing/oxidizing conditions. Similar phenomena were also observed for 30 mol.%

Ca substituted strontium molybdate by comparing freshly prepared $Sr_{0.7}Ca_{0.3}MoO_3$ of Figure 3-7b with the one in Figure 3-7c after one redox cycle. As shown in Figure 3-7a and 3-7d, $Sr_{0.7}Ca_{0.3}MoO_3$ can also be re-oxidized back to its oxidizing state, evidenced by the identical peak positions. The slightly broadened peaks could be ascribed to the decreased crystallinity caused by cyclic redox treatment.

Figure 3 - 7 XRD patterns of (a) $Sr_{0.7}Ca_{0.3}MoO_4$; (b) $Sr_{0.7}Ca_{0.3}MoO_3$; (c) $Sr_{0.7}Ca_{0.3}MoO_3$ after one redox cycle; (d) re-oxidized $Sr_{0.7}Ca_{0.3}MoO_4$ from (c).

To provide further support for molybdenum's dissolution back into the lattice, DSC-TGA analysis was conducted at the ramping rate of 15 °C/min to 900 °C. In Figure 3-8a, the TGA curves show two-stage weight increase, which correspond to two exothermic peaks in DSC plot in red arrows, especially for $Sr_{0.5}Ca_{0.5}MoO_3$. Clearly, weight starts to change around 400 °C, indicating the onset point of oxidation of $SCMO_{re}$ to $SCMO_{ox}$, reaches a saddle point at 600 °C in the case of $Sr_{0.5}Ca_{0.5}MoO_3$ and finally settles on a plateau above 800 °C. This behaviour presumably indicates the

Figure 3 - 8 (a) TGA-DTA curves of $\text{Sr}_{1-x}\text{Ca}_x\text{MoO}_3$ oxidation and the DSC curves are assigned accordingly in colours; (b) MoO_3 TGA in black squares and its DSC in red line (peaks of rising-up denoting exothermic, dropping-down as endothermic, indicated by pink arrows)

dissolution of metal Mo back to the lattice, in accordance with the second exothermic peak in DSC plot. However, as known that the melting point of MoO_3 is very low at $\sim 795^\circ\text{C}$ [247], it is possible for molybdenum to escape in the form of MoO_3 after oxidation in air at elevated temperature. To examine that, DSC-TGA curve of commercial MoO_3 is shown in Figure 3-8b. A typical endothermic peak emerges at $\sim 800^\circ\text{C}$, accompanied by a sharp decrease of weight, due to the sublimation of MoO_3 . This is in good agreement with a previous result [247]. In contrast, no endothermic

peak is observed for $\text{Sr}_{1-x}\text{Ca}_x\text{MoO}_3$ samples (Figure 3-8a, albeit the second exothermic peak of sample $\text{Sr}_{0.7}\text{Ca}_{0.3}\text{MoO}_3$ isn't obvious, yet still discernible around 800 °C). Instead, the weight starts to increase at around 400 °C and levels off at 800 °C. By referring to the following reaction:

We have calculated the weight increase of 7.3 wt.% and 7.7 wt.% for the oxidation of $\text{Sr}_{0.7}\text{Ca}_{0.3}\text{MoO}_3$ and $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_3$. These agree with what we have measured by TGA in Figure 3-8a. Based on the analysis above, we can conclude that $\text{Sr}_{1-x}\text{Ca}_x\text{MoO}_3$ ($x=0.3, 0.5$) is oxidized to $\text{Sr}_{1-x}\text{Ca}_x\text{MoO}_4$ ($x=0.3, 0.5$) from 400 °C to 800 °C through reaction (1). No evidence was found to be supportive for molybdenum sublimation in the form of MoO_3 . Instead, its oxidation and dissolution back into the lattice can be inferred, demonstrating the reversibility of Mo segregation.

3.3.3 Anode structure analysis and its electrochemical performance towards H_2 and CH_4

Figure 3-5d shows the cross-section view of SCMO_{ox} –GDC electrode after sintering at 1150 °C for 2 h. A porous anode of ~ 70 µm in thickness is well attached to LSGM electrolyte. Unlike previous studies, no buffer layer, *e.g.* LDC [281, 282] or SDC [118, 283] was used between anode and electrolyte in our study. By SEM, no obvious reactions can be discerned along the interface.

To test the effect of Mo on fuel oxidation, polarization curves were recorded at 800 °C on SCMO_{re} –GDC anode. After reduction in H_2 for 2 h to ensure the Mo ex-solution, increased performance towards H_2 oxidation can be obtained for $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_3$ –GDC compared to SrMoO_3 –GDC, 330 mW cm^{-2} vs. 280 mW cm^{-2} in Figure 3-9a, in accordance with the decreased polarization resistance (R_p) in Figure 3-9b, which implies that metal Mo does promote catalytic activity. A previous study reported a Ru

doped lanthanum chromite–GDC anode [284]. Its performance test in hydrogen for 96

Figure 3 - 9 (a) I-V-P curves for $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_3$ –GDC SrMoO_3 –GDC anodes at 800 °C in H_2 ; (b) their corresponding EIS curves.

h was observed 2 ~ 3 times better than that in hydrogen for 15 min because of the ripening of Ru nanoparticles in the course of time. However, our study showed that Mo ex-solution was much faster and these segregated Mo nanoparticles tend to agglomerate into larger particles of several tens of nano-meters, which possibly is the reason for the limited performance improvement.

3.4. Conclusions

Based on an electronic conductive anode material SrMoO_3 [1], we demonstrated a method for performance improvement by partially substituting Ca for Sr on the A site.

The Ca substitution decreased the thermodynamic stability upon reducing conditions, resulting in Mo segregation on the surface. We further confirmed this Mo segregation was reversible in response to reducing and oxidizing conditions. This ex-soluted Molybdenum showed its catalytic activity towards H_2 oxidation and C-H bond breaking. For H_2 oxidation, the performance was improved from 280 mW cm^{-2} to 330 mW cm^{-2} at $800\text{ }^\circ\text{C}$ when 50 mol.% Ca was incorporated. This study demonstrates for the first time that A-site substitution can also lead to B-site metal ex-solution and it differentiates from the previously reported B-site doped anodes with reversible metal ex-solution on B site, which enlightened a new thought to manipulate B-site through A-site doping.

Chapter 4 Investigation of molybdenum carbide nano-rod as an efficient and durable electrocatalyst for hydrogen evolution in acid and alkaline

(This chapter is reproduced with permission from P. Xiao, Y. Yan, X. Ge, et al., *Investigation of molybdenum carbide nano-rod as an efficient and durable electrocatalyst for hydrogen evolution in acidic and alkaline media*. Applied Catalysis B: Environmental, 2014. **154–155**(0): p. 232-237. Copyright 2014, Elsevier)

4.1. Introduction

Hydrogen production from electrochemical splitting of water has attracted increasing interests because it can be realized through renewable pathways [285]. Besides, the zero emission of carbonaceous species from hydrogen utilization makes hydrogen an ideal candidate for the replacement of fossil fuel energy in the future [2, 286]. In the course of seeking of highly efficient electrocatalyst for hydrogen production, Pt has emerged as the most efficient one in acidic media [287-290]. Unfortunately, the scarcity and high cost of Pt hinder its commercial application in large scale. In the past decades, efforts have been made to search for low-cost alternatives to reduce the use of Pt or even replace it [291]. Several non-noble metal based materials, such as transition-metal complexes [292, 293], chalcogenides [125, 154], carbide [190, 294, 295] and metal alloys [296] have been vigorously pursued as catalysts or supports for the electrochemical hydrogen evolution reaction (HER). Among them, molybdenum disulphide was highlighted as a superb and cost-effective catalyst [145, 161, 164, 167, 174], after polygonal molybdenum disulphide (MoS_2) nanocrystal with exposed edges on Au was found to be active towards HER [126, 173] for the first time. However, apart from its instability in alkaline condition [190], the conductivity of MoS_2 is very low, ranging from ca. 10^{-8} S/cm [297] to 0.1 S/cm [298], which usually requires the

additional incorporation of conductive substrates, such as graphene [134, 136, 141], carbon sphere [147], and carbon nanotubes [144].

Molybdenum carbide (Mo_2C), another type molybdenum compound, was widely employed as a catalyst for methane reforming [299], methanol steam reforming [300], oil conversion [301], and water gas shift reaction [302] etc. Its electrochemical activity towards HER was only recently reported by Hu et al. [190, 197]. Its derivatives, such as $\text{Mo}_2\text{C}/\text{CNT}$ [191] and $\text{Mo}_2\text{C}/\text{RGO}$ [193] also exhibit high activities towards hydrogen evolution. As a sole catalyst towards hydrogen evolution, catalytic activity and electrical conductivity are two critical factors for electrochemical applications. For Mo_2C , those two attributes have not been fully unveiled yet, especially in alkaline condition.

In this work, we synthesize Mo_2C nano-rods through a simple method of carburization of ammonium molybdate tetrahydrate and aniline complex [303, 304]. A well-defined porous Mo_2C nano-rod with highly exposed (101) plane was obtained at 700 °C under 20% H_2/Ar , and the composition transformations during carburization process are carefully studied. The activities of molybdenum carbides towards HER were investigated in both acidic and alkaline media.

4.2. Experimental

4.2.1. Mo_2C nano-rods synthesis

Ammonium molybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$) (Sigma-Aldrich) was used as the Mo precursor. Aniline (Sigma-Aldrich, >98%) was used as received. In a typical procedure, 0.827 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ was dissolved by 10 ml DI-water in a vial, and 1.089 ml aniline was pipetted into the solution. The pH value of the solution was adjusted to ~ 4.5 by stepwise dropping 1 M HCl under vigorous stirring. Finally, the obtained suspension in a vial was mounted in a water bathing receptacle at 80 °C for 3

h. After reaction, the yellowish product was washed by ethanol repeatedly. Before carburization, the as-synthesized Mo_2C nano-rod was dispersed into water for ultrasonication in a 15s-on-15s-off mode for 1 h and dried at 80 °C overnight. Carburization experiments were carried out at different temperatures (450 °C ~ 700 °C) in various gas compositions. Nickel was loaded onto Mo_2C rod by impregnation of 1 M $\text{Ni}(\text{NO}_3)_2$ and post-sintered at 450 °C under reducing condition.

4.2.2. Material characterization

X-Ray diffraction (XRD) was conducted using a $\text{Cu K}\alpha$ radiation source (Bruker, D2 Phaser) to examine the phase structures after carburization. Morphological contrasts were observed by using a field emission scanning electron microscope (FE-SEM, JEOL, JSM6701F, Japan) while transmission electron microscopy (TEM) and high resolution TEM images were collected on TEM Philips CM300. Raman spectroscopy spectrum was measured by a laser of 514 nm wavelength on the as-synthesized Mo_2C nano-rod. X-ray photoelectron spectroscopy (XPS) was performed on a VG Escalab 200i-XL spectrometer equipped with a monochromatic $\text{Al K}\alpha$ (1486.6 eV) X-ray source. The electrical conductivity tests were conducted using a four-probe method on a thin rectangular bar of dimensions 24 mm $\times$ 5 mm $\times$ 1 mm, which was uni-axially die-pressed under 300 MPa. Both Electrochemical Impedance Spectroscopy (EIS) and linear scanning voltammetry were applied to measure the conductivity. Polarization curves of the HER were collected by an Autolab PGSTAT302/FRA system (Eco Chemie, Netherland) in a three-electrode configuration at room temperature and Pt foil and Saturated Calomel Electrode (SCE) were used as the auxiliary electrode and the reference electrode, respectively. Firstly, SCE was calibrated by using Pt foil as the working electrode both in 0.5 M H_2SO_4 and 1 M KOH solution (See Figure 4-1) that was purged by N_2 for half an hour before the tests. Thus, all the potentials were

recorded with respect to the reversible hydrogen electrode (RHE). Catalyst ink was typically made by dispersing 3.5 mg of catalyst in 2 ml ethanol. After adding 0.5 ml of 0.05wt.% of Nafion solution (Gashub, Singapore) and ultrasonication, a certain amount of black slurry was pipetted onto the glassy carbon electrode (0.1963 cm²).

Figure 4 - 1 calibration of saturated calomel electrode in (a) 0.5 M H₂SO₄ and (b) 1 M KOH.

Current density was normalized to the geometrical area of the working electrode. Electrochemical impedance spectroscopy (EIS) was conducted in a potentiostatic mode in the frequency range of 10⁵ Hz to 0.1 Hz with a perturbation of 10 mV. At different overpotentials ($\eta=0 \sim 200$ mV), EIS curves were recorded. In particular, at $\eta=200$ mV, the obtained impedances were fitted by the Zview program. Tafel plots were drawn after *IR* compensation *i.e.* $\eta_{cor} = \eta - jR_{cor} = a + b \ln j$, where η (V) denotes the experimental potential applied vs. RHE, η_{cor} (V) as the *IR* compensated potential, b (mV dec⁻¹) as the Tafel slope, j (mA cm⁻²) as the normalized current density, and R_{cor} can be obtain from Nyquist plot.

4.3. Results and discussion

4.3.1. Phase transition from molybdenum complex to Mo₂C nano-rod and its morphology

Through a self-assembly method to attach protonated aniline to trimolybdate anions [305, 306], anisotropic growth [304] of anilium trimolybdate forms 1D nano-rods at 80 °C. The as-prepared precursor was firstly annealed in pure H₂ for 1 h at the temperature ranging from 450 °C to 700 °C. The corresponding XRD patterns are shown in Figure 4-2. At 450 °C, Mo₂N phase is observed (Figure 4-2c), but the

Figure 4 - 2 XRD patterns of molybdates: a) 450 °C, pure H₂; b) 600 °C, pure H₂; c) 700 °C, pure H₂; d) 700 °C, 50 vol.% H₂/Ar; e) 700 °C, 35 vol.% H₂/Ar; f) 700 °C, 20 vol.% H₂/Ar.

crystallinity is fairly low and the calculated particle size is ~3.4 nm from the Scherrer's equation. When the temperature is raised up to 600 °C, Mo₂C phase emerges as shown in Figure 4-2b, but a hump of an unknown impurity at around 30 ° can be discerned. With the further increase of temperature to 700 °C (Fig. 1a), Mo₂C phase (JCPDS 35-0787) stands out, but a new peak emerges at 40.5 ° that is indexed to metallic Mo. Hence, 50 vol.%, 35 vol.% and 20 vol.% of H₂ balanced by argon are fed, and lead to a decreased content of Mo in Mo₂C accordingly as shown in Figure 4-2(d, e, f). To be specific, the Mo₂C obtained in 50 vol.% H₂/Ar and 35 vol.% H₂/Ar are denoted HMo-Mo₂C-R, LMo-Mo₂C-R, respectively, whereas the samples obtained in 20 vol.% H₂/Ar

show no diffraction signal of metallic Mo and are named as Mo₂C-R. Then FE-SEM was employed to examine the morphology contrast among HMo-Mo₂C-R, LMo-Mo₂C-R and Mo₂C-R. Clearly, both HMo-Mo₂C-R and LMo-Mo₂C-R show rough surfaces embedded with small particles (Figure 4-3), and XRD patterns suggest that those particles should be metallic Mo, corresponding to the peak emerging at 40.5 °in

Figure 4 - 3 FESEM images (a) HMo-Mo₂C-R; (b) LMo-Mo₂C-R.

Figure 4-2(c, d, e). In sharp contrast, Mo₂C-R exhibits smooth surface with a rod diameter of ~50 nm to ~ 200 nm in Figure 4-4a. TEM images showed in Figure 4-4b reveal a porous structure of the synthesized Mo₂C nano-rods, consistent with a previous study [303]. From Figure 4-4c, groups of parallel lines are observed for the first time. Figure 4-4d suggests that those lines are arrayed with (101) plane of Mo₂C with a *d*-space of 0.23 nm, which can be detected in several particles. Besides, Figure 4-4d also shows that this porous Mo₂C nano-rod is comprised of rather small particles, and the inset of Figure 4-4c shows the particle size distribution.

X-ray photoelectron spectroscopy (XPS) was employed to further elucidate the composition of Mo₂C-R. HMo-Mo₂C-R was also examined for the purpose of comparison. As shown in Figure 4-5, both deconvoluted profiles of Mo₂C-R and HMo-Mo₂C-R show MoO₃ and MoO₂ [190, 307, 308], suggesting that Mo₂C is prone

to oxidation on the surface. Figure 4-5b also reveals that HMo-Mo₂C-R includes a doublet of 227.7eV/230.8eV, which can be ascribed to the metallic Mo decorated on Mo₂C, while no metallic Mo is observed on Mo₂C-R sample, in accordance with XRD results.

4.3.2. Electrochemical, conductivity test

Figure 4 - 4 Morphology of Mo₂C-R (a) FESEM images; (b, c, d) TEM images.

Before the measurement of conductivity, Raman spectroscopy experiments were conducted for further confirmation of the residue carbon that the as-prepared Mo₂C-R may retain during carburization. As shown in Figure 4-6, no characteristic peaks, *e.g.* the D band, G band or 2D band [309, 310] of carbon materials are detected, instead it

Figure 4 - 5 XPS of (a) $\text{Mo}_2\text{C-R}$; (b) $\text{HMo-Mo}_2\text{C-R}$

Figure 4 - 6 Raman spectrum of $\text{Mo}_2\text{C-R}$ and $\text{HMo-Mo}_2\text{C-R}$

only manifests typical peaks of Mo_2C [311]. The electrical conductivity of Mo_2C is critical for electrocatalytic application and was measured at room temperature. The results from both EIS and I-V measurement agree with each other quite well, rendering 30 S cm^{-1} (Figure 4-7). This value is comparable to those commonly used substrates,

Figure 4 - 7 Conductivity measurements of as-synthesized Mo₂C-R

such as RGO, which has a reported range of $0.5 \text{ S cm}^{-1} \sim 100 \text{ S cm}^{-1}$ [309, 312]. It is noteworthy that the conductivity test may not fully exhibit its theoretical value as the die-pressed Mo₂C-R bar is still porous, which definitely underestimates its conductivity [313, 314]. This indicates that Mo₂C nano-rod itself has sufficient conductivity for electrocatalytic application.

In a three-electrode configuration, linear scan voltammetry (LSV) experiments were firstly conducted in 0.5 M H₂SO₄. As shown in Figure 4-8, all the as-synthesized molybdenum carbide nano-rods outperform commercial Mo₂C, and among them, Mo₂C-R exhibits the highest catalytic activity. The onset potentials for HMo-Mo₂C-R, LMo-Mo₂C-R and Mo₂C-R can be discerned as 125 mV, 97 mV and 68 mV respectively, which are determined by reading the deviating point in the potential-log $|j|$ plot (Figure 4-9) [141, 287].

Figure 4 - 8 Polarization curves in 0.5 M H₂SO₄, mass loading 0.43 mg cm⁻²

For Mo₂C-R, the potential of $\eta=200$ mV drives current densities of 32 mA cm⁻² vs. 0.8 mA cm⁻² for commercial Mo₂C, suggesting a promising candidate for hydrogen evolution. Compared to commercial Mo₂C, this high performance is benefitted from small particulates among the porous structures observed in TEM images (Figure 4-4) as this porous structure potentially increases the accessibility of protons to the inner particles. Interestingly, among the as-synthesized Mo₂C rods, the cathodic current drops with the increased content of metallic Mo in the catalysts. This phenomenon strongly indicates that metallic Mo is responsible for this distinguishable performance. A theoretical calculation [125, 315] of the binding energy of metallic Mo implies that metal Mo is not a good candidate for hydrogen evolution because of its strong bond to

Figure 4 - 9 Tafel plots of commercial Mo₂C, Mo₂C-R, HMo-Mo₂C-R, LMo-Mo₂C-R, 20% Pt/C in 0.5 M H₂SO₄.

atomic H. Likewise, a slow H release caused by the strong hydrogen bond could explain the inferior performance of HMo-Mo₂C-R and LMo-Mo₂C-R to Mo₂C-R. Furthermore, the XPS spectra deconvolution shows that the carbide peak of HMo-Mo₂C-R is relatively weaker than that of Mo₂C-R (magenta line, Figure 4-5). A higher intensity indicates a higher content of Mo₂C for the porous Mo₂C-R compared to HMo-Mo₂C-R and LMo-Mo₂C-R. This correlates well with their HER activity and suggests Mo₂C phase is responsible for the catalytic activity towards hydrogen evolution.

To understand various processes during HER, Electrochemical Impedance Spectroscopy (EIS) was carried out under different overpotentials. At $\eta=0 \sim 100$ mV, Bode plots suggest a one-time-constant process for both LMo-Mo₂C-R (Figure 4-10b)

and Mo₂C-R (Figure 4-11b). Nyquist plot also confirms this behaviour of Mo₂C-R, indicated by one semi-circle, as shown in Figure 4-11a. Interestingly, when the overpotential is increased up to $\eta = 150$ mV and 200 mV, it is found that a linear part

Figure 4 - 10 Bode plots in 0.5 M H₂SO₄ under different overpotentials: (a) HMo-Mo₂C-R; (b) LMo-Mo₂C-R

emerges at high frequency which is associated with the transport process [169]. Low-frequency region is highly potential-dependent by comparing Figure 4-11c with d, suggesting a charge-transfer process. Hence, a model of a R_s representing the ohmic

Figure 4 - 11 EIS curves in 0.5 M H₂SO₄: (a) Nyquist plot and (b) Bode plot of Mo₂C-R; (c) Nyquist plots of LMo-Mo₂C-R and Mo₂C-R at $\eta = 150$ mV; (d) Nyquist plots of LMo-Mo₂C-R, Mo₂C-R and their fitting results at $\eta = 200$ mV.

resistance of electrolyte and all contact resistances, in series with a Constant Phase Element (CPE) that is in parallel with a Warburg resistance (W_s) and a charge-transfer resistance (R_{ct}) (see the model in Figure 4-12), is applied and the R_{ct} and Warburg

Figure 4 - 12 Randles' circuit as the equivalent model

$$\text{Warburg impedance } Z = \frac{R_w \tanh[(jT_w \omega)^{p_w}]}{(jT_w \omega)^{p_w}}$$

resistance (R_w) of the fitted results are presented in Table 4-1. As shown in Figure 4-11d, it is clearly that Mo₂C-R (R_{ct} , 1.4 Ω ; R_w , 3.9 Ω) shows a faster charge-transfer and diffusion process than LMo-Mo₂C-R (R_{ct} , 4.9 Ω ; R_w , 6.9 Ω) at $\eta = 200$ mV. In contrast, HMo-Mo₂C-R exhibits one-time-constant behaviour at all potentials applied (Figure 4-10a).

Table 4 - 1 Tafel slope b , exchange current density j_o in 0.5 M H₂SO₄

	b (mV dec⁻¹)	j_o (mA cm⁻²)	R_{ct} @ $\eta = 200$ mV (Ω)	R_{ws} @ $\eta = 200$ mV (Ω)
Mo₂C-R	58	3.3×10^{-2}	1.4	3.9
LMo-Mo₂C-R	70	3.1×10^{-2}	4.9	6.9
HMo-Mo₂C-R	74	1.5×10^{-2}	11.6	—
Commercial Mo₂C	73	1.4×10^{-3}	—	—
20 wt.% Pt/C	32	0.62	—	—

At low current density, where mass transport is negligible, Tafel analysis can be applied to analyse the reaction mechanism. The detailed Tafel slopes and exchange current densities are summarised in Table 4-1. The Tafel slopes of 66 mV dec⁻¹ and 58 mV dec⁻¹ (IR drop corrected) for Mo₂C-R were observed, which is comparable to the previously reported values of 55 mV dec⁻¹ for Mo₂C-CNT [191] and

62.7 mV dec⁻¹, for MoSoy/RGO [193]. Generally, to convert protons to H₂, three elementary reaction steps are involved [148], Volmer: H⁺ + e⁻ → H_{ad} (1), Heyrovsky: H_{ad} + H⁺ + e⁻ → H₂ (2) and Tafel: H_{ad} + H_{ad} → H₂ (3). Molecular hydrogen can be produced when reaction (1) is combined with reaction (2), or reaction (3). If the Volmer step is the rate-determining step, it invokes a Tafel slope of 120 mV dec⁻¹. If the Heyrovsky or Tafel reaction is the rate-determining step, it gives a Tafel slope of ~40 mV dec⁻¹ or ~30 mV dec⁻¹ respectively. In our study, a Tafel slope of ~58 mV dec⁻¹ or Mo₂C-R implies the Volmer-Heyrovsky mechanism. By extrapolating the linear part of the potential-log|j| plot at η=0 (Figure 4-9), the exchange current density can be obtained (Table 4-1). In contrast to commercial Mo₂C, the exchange current densities of all the as-synthesized nano-rod catalysts are found in the order of magnitude of ~10⁻² mA cm⁻² and are comparable to the hybrid Mo₂C-CNT, 1.4 × 10⁻² mA cm⁻² and MoSoy/RGO, 3.7 × 10⁻² mA cm⁻² [193]. These values are higher than molybdenum disulphide [149, 158, 160], suggesting its promising activity towards HER as a standalone catalyst.

Stability is a key factor for evaluating a catalyst. Long-term stability was tested by cycling potential from -0.24 to 0 V v.s. RHE. As shown in Figure 4-13, there is a slight

Figure 4 - 13 Stability test of Mo₂C-R in 0.5 M H₂SO₄, scanning rate: 100 mV s⁻¹

decay of current density in the first 1000 cycles, but it retains its activity in the second 1000 cycles, which demonstrates an excellent cycling life in acidic environment.

Few catalysts can be employed in both acid and alkaline media. Noble metal Pt is one of them. Previously, non-noble commercial Mo_2C was proposed as a catalytic candidate for hydrogen evolution in basic conditions by Hu et al. [190]. In this study, we also examined the HER activity of the porous Mo_2C nano-rod in high pH condition. It was observed that the current density reaches $\sim 30 \text{ mA cm}^{-2}$ at $\eta = 200 \text{ mV}$ as shown in Figure 4-14, exhibiting an advantageous performance over commercial Mo_2C (0.5 mA cm^{-2} at $\eta = 200 \text{ mV}$). However, it still lacks competition compared to Pt catalyst as a non-noble catalyst, especially in view of the onset potential; $\sim 67 \text{ mV}$ vs. nearly zero for Pt in Figure 4-14, which implies that a higher potential is needed to drive HER.

Figure 4 - 14 Polarization curves of various catalysts in 1 M KOH solution.

Nickel as a cheap metal has been widely explored for hydrogen evolution in concentrated alkaline media. The low overpotential, high exchange current density [316, 317], especially in nano-powder [296] make nickel a competitive catalyst for HER. Therefore, Ni is incorporated into the Mo_2C nano-rod to form the Ni supported Mo_2C -R, denoted Ni- Mo_2C -R (Figure 4-15). With increased loading of Ni, the onset

potential decreases. In particular, when the loading amount is up to 30 wt.%, the onset

Figure 4 - 15 (a) 10 wt.% Ni loading on Mo₂C-R; (b) 30 wt.% Ni loading on Mo₂C-R

potential cannot be discriminated from Pt in Figure 4-14. However, it compromises with higher overpotential at high cathodic current density. The Tafel slope b and current densities are summarized in Table 4-2, where Mo₂C-R shows a Tafel slope of 45 mV dec⁻¹ with the exchange current density of 1.1×10^{-2} mA cm⁻², similar to its performance in acid. It is also observed that the exchange current density increases with the increased loading of Ni.

Table 4 - 2 Tafel slope b , exchange current density j_0 in 1 M KOH

	b (mV dec ⁻¹)	j_0 (mA cm ⁻²)
Mo₂C-R	45	1.1×10^{-2}
3 wt.% Ni-Mo₂C-R	55	3.9×10^{-2}
10 wt.% Ni-Mo₂C-R	73	0.14
30 wt.% Ni-Mo₂C-R	49	0.27

However, the Tafel slope is not subjected to the same tendency. In the perspectives of elementary steps of hydrogen evolution, it is possible that Ni promotes the adsorption of H species, compared to pure Mo₂C-R due to its strong bond to H [125]. Thus, it could explain the increased exchange current density and decreased onset potential. On the other hand, it hampers the H_{ad} or molecular H₂ release from the active sites, and

furthermore, high loading of Ni may occupy part of the active sites or the pathways for H^+ to access Mo_2C -R on the surface (Figure 4-15b). This could give explanation to the decreased current density when high content of Ni was incorporated and also expounds the changes of Tafel slope because of the ambivalent effects invoked by Ni. However, the detailed mechanism of decreased onset potential and degraded performance at high current density is not fully understood at this stage and future experiments are needed for further clarification.

4.4. Conclusions

In summary, we have successfully synthesized Mo_2C nano-rods through facile carburization of anilinium molybdate. The excellent electrocatalytic performance towards hydrogen evolution was observed in both acid (32 mA cm^{-2} , at $\eta = 200\text{ mV}$) and alkaline media (30 mA cm^{-2} , at $\eta = 200\text{ mV}$) as a non-noble catalyst. Tafel slopes of 58 mV dec^{-1} in acid and 45 mV dec^{-1} in alkaline, suggest a Volmer-Heyrovsky rate-determining mechanism. The performance is originated from the high conductivity and well-defined, porous morphology. Incorporation of Ni onto Mo_2C nano-rods reveals that Mo_2C lacks adsorptive bonding to H species at low overpotentials compared to metal Ni, thus causing high onset potential. More importantly, the incorporation of Ni onto Mo_2C nano-rods reveals the discrepant nature of metals *e.g.* Ni and compounds, *e.g.* Mo_2C for hydrogen evolution. It illuminates the possible ways for further improvement of the performance by incorporating Ni into carbide to nickel molybdenum carbide complex or their hybrids.

Chapter 5 Synthesis and electrochemical activation of molybdenum tungsten carbide nanowires for efficient and stable hydrogen evolution

5.1. Introduction

With zero carbon emission, hydrogen is envisioned as a promising energy carrier [2] to substitute for fossil fuels in future. Hydrogen production through electrochemical water-splitting has been regarded as a promising way for large scale hydrogen production on the condition that the required electricity comes from renewable energies [175]. Towards that end, the key challenge lies in the development of low-cost, highly efficient electro-catalyst to accelerate the electrochemical process of hydrogen evolution reaction (HER). Pt-group metals emerge as the most efficient candidates, but the high cost and scarce reserve on the Earth exclude the possibility of using them for practical applications. Recently, the search of non-noble metal based catalysts reveals that some earth-abundant transition-metal sulphides [126, 142, 145, 149, 154, 164, 165, 167, 169, 173, 174, 318], selenides [159, 319, 320], carbides [190, 191, 193, 197, 321, 322], nitrides [224, 287] and phosphides [205, 207, 323, 324], exhibit promising electrocatalytic activities towards HER. For the well-developed MoS_x system [176, 177], previous efforts have been focused on the synthesis of amorphous phase [164, 165, 168], and scaling down to nanostructured MoS_x from its bulk term, *e.g.* thin-layered nanoplates [150-152] for the benefit of the abundantly exposed S-edges. However, considering the low crystalline state of amorphous molybdenum sulfide, poor long-term stability is expected due to the possible dissolution of amorphous MoS_x back to [MoS₄]²⁻ in the solution [164]. Besides, the intrinsic low electrical conductivity of MoS₂ (10⁻⁸ S/cm [297] to 0.1 S/cm [298]) is still a big barrier to overcome before any commercial application becomes possible. Other than sulfide, highly crystalline molybdenum carbide appears a promising candidate as

it exhibits certain activity towards HER even in bulk phase [190] and it possesses an advantageous conductivity ($\sim 30 \text{ S cm}^{-1}$) over MoS_2 [325]. A recent work [197] also demonstrated that improved performance was obtained by introducing a mesoporous structure, which sheds light on greatly improving the HER performance by designing novel nanostructure and increasing surface area. Unfortunately, it is not easy to obtain controlled nanostructure as carbides are usually synthesized by high temperature carbonization process. Besides, a surface carbon layer normally forms during carbonization and subsequent activation is needed to remove this carbon layer. Such activated Mo_2C is prone to oxidation on the surface even in ambient air, as manifested by pronounced XPS peaks [325] in high binding-energy zone, especially in aged sample. Given above, to synthesize well-defined nanostructured Mo_2C based material with superior stability in air and superb activity towards HER is still challenging and its success may truly open up a new direction for the development of none-noble metal based electro-catalyst for water electro-splitting.

Herein, we report a novel binary catalyst that consists of Mo_2C and WC in a well-defined nanowire structure. Based on a tungsten trioxide precursor, molybdenum is successfully integrated onto it by a hydrothermal method. A subsequent facile carburization transforms oxide to carbide, with preserved interwoven nanowire structure. The obtained binary system shows excellent activity and stability towards the HER, featuring that: (1) enhanced conductivity is expected by introducing highly conductive WC as one constituent; (2) there is no need to form single-layer or thin-layer nanostructure to ensure high conductivity as in the case of MoS_2 ; (3) nanostructured Mo_2C is highly integrated onto nanowire, achieving atomic affinity to WC and ensuring high structural stability; (4) electrochemical activation by cyclic

voltammetry induces a hydrophilic interface of the catalyst by introducing carboxyl/epoxy groups, which facilitates the HER.

5.2. Experimental

5.2.1 Materials and methods

Ammonium molybdate tetrahydrate, $((\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O})$, Sigma-Aldrich, Bioultra, >99.0%), sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$, Sigma-Aldrich, $\geq 99\%$) are used as received and no further purification experiments are conducted. In the hydrothermal method, stoichiometric $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and $\text{Na}_2\text{WO}_4\cdot 4\text{H}_2\text{O}$ (e.g. 4:1 in molar ratio for nw-W4MoC) were dissolved in DI-water and adjust the pH value to ~ 3 by step-wisely adding 5 M HCl, followed by the hydrothermal reaction in autoclave at $180\text{ }^\circ\text{C}$ for 10 h. After washing the resulting sample collected from autoclave, the obtained bluish powder is undergoing carburization in a tubular furnace at $850\text{ }^\circ\text{C}$. Note that no further deactivation is needed. WC, and nw-W2MoC are synthesized in the similar procedure, and Mo_2C is obtained from carburizing commercial MoO_3 .

5.2.2 Materials characterization

X-Ray diffraction (XRD) with a Cu $\text{K}\alpha$ radiation source (Bruker, D2 Phaser) was used to examine the crystal structures of the as-synthesized WC, Mo_2C , nw-W2MoC and nw-W4MoC. For Morphology, a field emission scanning electron microscope (FE-SEM, JEOL, JSM6701F, Japan), transmission electron microscopy (TEM, Philips CM300) coupled with Energy dispersive X-ray spectroscopy (EDS) were employed. To examine the composition, X-ray photoelectron spectroscopy (XPS) experiments were performed on a VG Escalab 200i-XL spectrometer equipped with a monochromatic Al $\text{K}\alpha$ (1486.6 eV) X-ray source. Electrode preparation and electrochemical measurements Raman spectroscopy spectrum was measured by a

laser of 514 nm wavelength.

Catalyst ink was typically made by dispersing 14 mg of catalyst in 2 ml ethanol. After adding 0.5 ml of 0.05 wt.% of Nafion solution (Gashub, Singapore) and ultrasonication, an aliquot of 5 μL was pipetted onto the glassy carbon electrode (0.1963 cm^2) to reach the catalyst loading of 1.28 mg cm^{-2} . In a three-electrode configuration, Polarization curves were collected by an Autolab PGSTAT302/FRA system (Eco Chemie, Netherland) at room temperature. Carbon rod and Saturated Calomel Electrode (SCE) are used as the auxiliary electrode, the reference electrode, respectively. All the potentials shown were recorded with respect to the reversible hydrogen electrode (RHE) after IR correction unless it is denoted individually, where the R is referred to the ohmic resistance arising from the electrolyte/contact resistance of the setup, and measured by Electrochemical impedance spectroscopy (EIS). Current density was normalized to the geometrical area of the working electrode. Polarization data is collected at the scan rate of 2 mV/s on a rotation disk electrode under 2000 rpm. EISs were carried out in a potentiostatic mode in the frequency range of 10^5 Hz to 0.1 Hz with the amplitude of 10 mV . At different overpotentials ($\eta = 90 \sim 120\text{ mV}$ with an interval of 10 mV), EIS curves were taken.

5.2.3 Measurements of the weight ratio in the binary carbides

nw-W₂MoC and nw-W₄MoC consist of Mo₂C and WC. The oxidation in air at high temperature ($800\text{ }^\circ\text{C}$) leads to the formation of WO₃ and MoO₃, and MoO₃ has low melting point ($\sim 795\text{ }^\circ\text{C}$), causing a quick sublimation around $800\text{ }^\circ\text{C}$ [247, 275]. So, isothermal treating of the sample at $850\text{ }^\circ\text{C}$ for 2 h ensures the complete sublimation of MoO₃, shown in the blue curve that track the weight change of the sample in the course of time. The final chemical formula in terms of the molar ratio is determined as

$W_{0.62}Mo_{0.38}C$ and $W_{0.27}Mo_{0.73}C$ via this method, respectively for nw-W2MoC and nw-W4MoC.

5.3. Results and discussion

The well-defined nanowire structure of complex molybdenum tungsten carbide is realized by a pseudomorphic transformation of molybdenum tungsten oxide. First, based on the knowledge that hexagonal WO_3 nanowire can be formed via a sulfate ion

Figure 5 - 1 morphology of synthesized (a) WO_3 nanowire; (b) nw-W4MoO₃; (c) nw-W4MoC; (d), (e), (f): TEM images of nw-W4MoC; (g) Mo K α 1, and (f) W L α 1: TEM-EDX mapping with respect to the area in (f).

directing growth mechanism [326] (Figure 5-1a), adding $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ together in the process allows the formation of nanowires of molybdenum tungsten complex oxides, as shown in Figure 5-1b (W: Mo = 1:4 in molar ratio), while using $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ alone only leads to the formation of micro-belt of MoO_3 (not shown). To our observation, changing the molar ratio of the precursor doesn't lead to any morphology change as shown in Figure 5-2 (W: Mo = 1:2 in molar ratio). For the sake of convenience, the samples are termed by the

Figure 5 - 2 SEM graph of nw-W₂MoO₃

nominal molar ratio of W to Mo in the precursor. So, the nanowires of molybdenum tungsten complex oxides in a molar ratio of 1:2 and 1:4 (W: Mo) are termed as nw-W₂MoO₃ and nw-W₄MoO₃, respectively. The carbides of their counterparts are named as nw-W₂MoC and nw-W₄MoC. After carburization, the nw-W₄MoC and nw-W₂MoC retain their structure of interwoven nanowires, with an average size of 15-20 nm (Figure 5-1c, Figure 5-1d and Figure 5-3). In contrast, WC failed to retain the morphology of nanowire WO₃ and exists as interconnected particles (Figure 5-4), and this is possibly due to the enhanced tolerance of sintering at high temperature with the addition of molybdenum. In a sense, the formation of such binary carbide nanowire is

Figure 5 - 3 SEM images of nw-W₂MoC

unique as single element carbide cannot be formed following the same approach. High magnification TEM image in Figure 5-1e reveals that 2~3 layers of carbon wrap on the

Figure 5 - 4 SEM image of WC

surface of nanowires, which is commonly detected for carbides undergoing carburization in hydrocarbons [327]. More importantly, nanoparticles of Mo₂C are found both on the surface and integrated into the nanowire structure, with highly exposed (101) planes. A uniform distribution of Mo₂C and WC is observed along the nanowires by TEM-EDX mapping in a small region in Figure 5-1f. The investigation of surface area through N₂ adsorption/desorption gives a Brunauer–Emmett–Teller (BET) surface area of 44 m²/g (Figure 5-5) which is comparable to the mesoporous

Mo₂C [197]. But the key difference is that the surface areas in this case are mostly

Figure 5 - 5 BET surface area of nw-W4MoC

external surface area while that the mesoporous one is mainly contributed by inner pore surfaces and is less accessible for subsequent electrochemical reaction.

The crystal structures of the samples are examined by XRD. As shown in Figure 5-6a and 5-6b, the peaks of single WC and Mo₂C are in hexagonal pack, belonging to the

Figure 5 - 6 XRD of (a) WC.; (b) Mo₂C; (c) nw-W2MoC; (d) nw-W4MoC.

space group of P-6m2 (187) and P63/mmc (194), respectively. However, in the binary system of nw-W₂MoC and nw-W₄MoC, faced-centered cubic phase of WC (β -WC, *i.e.* WC_{1-x}, in contrast to hexagonal WC, *i.e.* α -WC) is also observed, especially in the case of nw-W₄MoC with high Mo content, where α -WC phase completely disappears and gives rise to β -WC, and the characteristic peak of β -WC at 42.9 ° shifts to 41.6 ° (labelled in green dot), indicating the possible dissolution of Mo atoms into WC lattice [321], causing increased distance of lattice planes in the crystal structure. To probe the surface property, X-ray photoelectron spectroscopy (XPS) was employed. Figure 5-7a, Figure 5-7b and Figure 5-7c show the typical XPS profiles of pristine nw-W₄MoC. The Mo 3d electron (Figure 5-7a) displays two doublets. After peak deconvolution, the

Figure 5 - 7 XPS of nw-W₄MoC sample: before activation (a) Mo 3d; (b) W 4f; (c) C 1s; After electrochemcail activation (d) C1s.

pair of peaks (228.8 eV/231.9 eV) in higher binding energy is attributed to Mo^{4+} or MoO_2 [328, 329], while the other pair is assigned to Mo_2C . No peaks representing higher valence state, *e.g.* Mo^{5+} , Mo^{6+} or MoO_3 , are detected. We speculate that the carbon on the surface may have prohibitive effect to prevent further oxidation, explaining the absence of the peaks $\text{Mo}^{6+}/\text{MoO}_3$ that is observed in our previous study [325]. Similarly, W4f electron shows strong signal in a doublet (31.5/33.65 eV) in Figure 5-7b, which represents the characteristic peaks for WC [187]. A small shoulder profile is also detected in the region of high binding energy ($\sim \text{WO}_x$), indicating a minor oxidation of WC, likewise Mo_2C . However, C1s profile only manifests the graphitic carbon ~ 284.3 eV [187], and no carbidic peak (lower binding energy, ~ 282.7 eV [187]) is observed. This can be ascribed to the carbon on the surface, where the graphitic carbon has covered the signal of the carbidic carbon. A similar phenomenon is observed by Chen et al. [187], where the graphitic carbon layers are even detectable by XRD if they are thick enough. Nevertheless, our study doesn't show any diffraction peaks from graphitic carbon by XRD, suggesting the thin thickness of the carbon layer.

The activities of the various catalysts are investigated in 0.5 M H_2SO_4 in a three-electrode setup (Figure 5-8). To avoid any possible contamination of Pt, carbon rod is used as the counter electrode (see supporting information (SI) for the details). By comparing the catalysts synthesized, we can conclude that the activity in the pristine bimetallic carbide is higher than any single metallic carbide and such activity is mostly originated from Mo_2C [186, 190], lying in the fact that Mo_2C obtained from commercial MoO_3 (bulk phase) outperforms WC in nanosize (Figure 5-4) and increased content Mo from nw-W2MoC to nw-W4MoC results in improved

performance (the weight ratio of W/Mo is determined by TGA in Figure 5-9 and discussed in details in experimental section 5.2.3). This improved performance relative to single phase Mo_2C emphasizes the benefit of such unique structure that allows the

Figure 5 - 8 polarization curves of molybdenum tungsten carbide (scan rate: 2 mV/s): (a) before CV activation, (c) after CV activation; Tafel plots: (b) before CV activation, (d) after CV activation.

dispersion and integration of Mo_2C in the highly conductive WC nanowire support ($\sim 10^5 \text{ S/cm}$ at 20°C). Another useful metric to interpret the polarization curve is through the comparison of Tafel slope by plotting potential vs. $\log |j|$ (current density in logarithm). By applying Volmer-Tafel or Volmer-Heyrovsky mechanism, Tafel slope as a descriptor gives illustrative information for the comparison of the kinetic rate of the discharging reaction (Volmer step: $\text{H}_3^+\text{O} + e^- + \text{M} \rightarrow \text{H}_{\text{ad}}\text{-M} + \text{H}_2\text{O}$ [330]). Tafel slope of 82 mV dec^{-1} for WC suggests that it is inferior to Mo_2C (56 mV dec^{-1}), as shown in Figure 5-8b. The bimetallic carbide nanostructure doesn't change the

Figure 5 - 9 TGA of nw-W2MoC and nw-W4MoC

reaction route, indicated by the similar Tafel slope obtained ($\sim 56 \text{ mV dec}^{-1}$). In the meantime, even for the best performing catalyst (the pristine nw-W4MoC), the overpotential after iR correction still reaches 250 mV at 80 mA/cm^2 (Figure 5-8). This is likely due to the presence of surface carbon layer, as evidenced from the TEM and XPS analysis. It is possible to remove the extraneous carbon by cutting off the hydrocarbon after carburization, and feeding pure H_2 immediately, but it requires the precise control of the temperature, dwell time and hydrogen flows. Chen et al. [185] proposed the elimination of the carbon by exposing the catalyst in an oxygen plasma environment, which requires a plasma generator. In our study, we find that simple electrochemical activation by cyclic voltammetry (0.26 to 0.61V vs. RHE) in 1000 cycles could potentially serve the same purpose. Compared to the previous activation approaches, such electrochemical activation is very simple and does not need additional apparatus. The unique advantage is that it allows the in-situ activation at the device level after the catalyst is assembled into the device. After the activation, significant improvement in the activity can be observed. For example, to drive a current density of 80 mA cm^{-2} , it requires the overpotential of 184 mV (vs. 250 mV

before activation) for the sample of nw-W4MoC, and improved performance is also observed for Mo₂C and nw-W2MoC as shown in Figure 5-8c. The exchange current density extracted from the Tafel plot is summarized in Table 5-1, where nw-W4MoC shows 5 times increase in the exchange current density after the electrochemical activation ($2.9 \times 10^{-2} \text{ mA cm}^{-2}$ vs $4.7 \times 10^{-3} \text{ mA cm}^{-2}$). Electrochemical impedance

Table 5 - 1 Tafel slope b and exchange current density j_0

	Before activation		After activation	
	b (mV dec ⁻¹)	j_0 (mA cm ⁻²)	b (mV dec ⁻¹)	j_0 (mA cm ⁻²)
WC	82	6.8×10^{-4}	-	-
Mo ₂ C	58	2.6×10^{-3}	53	5.8×10^{-3}
nw-W2MoC	56	3.4×10^{-3}	53	1.1×10^{-2}
nw-W4MoC	56	4.7×10^{-3}	52	2.9×10^{-2}

spectra give similar information (Figure 5-10 and Table 5-2), where decreased charge transfer resistance (R_{ct}) is observed when the pristine nw-W4MoC is activated. Besides, a Tafel slope of 52 mV dec⁻¹ implies that the activated nw-W4MoC is subject to the same Volmer-Heyrovsky route. To our knowledge, this performance is the best

Table 5 - 2 charge transfer resistance of nw-W4MoC before and after cyclic voltammetry

	R_{ct} before activation (ohms)	R_{ct} after activation (ohms)
$\eta = 90 \text{ mV}$	390.5	118.0
$\eta = 100 \text{ mV}$	181.6	78.2
$\eta = 110 \text{ mV}$	133.8	49.5
$\eta = 120 \text{ mV}$	123.0	32.5

among all the carbide material investigated so far [190, 191, 193, 197, 321, 322]. To elucidate the activation process, the activated nw-W4MoC was characterized by XPS. Figure 5-7 shows that new peaks emerge in the profile of C1s after the activation. The peak in low binding energy (282.8 eV) is attributed to carbidic carbon, and the peaks in the region of high binding energy are signed to epoxy carbon, carboxyl group respectively [331, 332]. It is noteworthy that graphitic carbon is still present, but as a minor composition in the nw-W4MoC. Raman spectra in Fig. 5 evidence the graphene-like carbon in both the pristine and activated nwW4MoC by the presence of D band and G band that is correlated with E_{2g} mode of sp^2 carbon. But the signal is less prominent after the activation. Given the above, the carbon layer on the surface is

Figure 5 - 10 Bode and Nyquist plot of nw-W4MoC at different over-potentials in 0.5 M H_2SO_4

not completely stripped off by the CV technique. However, the electrochemical treatment successfully modified the interfacial properties by converting graphitic carbon into hydrophilic

carboxyl/epoxy radicals. We intuitively propose that the negative charged carboxyl/epoxy group may enhance the bonding to proton, and thus accelerate the diffusion of bound proton to the active site of Mo_2C , indicated by the decreased R_{ct} . This could explain the surprisingly increased performance. In a control experiment, we conducted the CV scans in a less positive potential window (0.26 to 0.46 V vs. RHE,

Figure 5 - 11 Raman spectra of nw-W4MoC

in Figure 5-12), and the result shows a higher activity than pristine nw-W4MoC, but inferior to that treated in the potential window of 0.26 V to 0.61V vs. RHE. Further

Figure 5 - 12 polarization curve by cyclic voltammetry at different potential window, (a) 0.26 V to 0.46 V vs. RHE; (b) 0.26 V to 0.61 V vs. RHE in 0.5 M H₂SO₄.

examination by XPS (Figure 5-13) reveals a lower relative intensity of carboxyl/epoxy group to carbidic carbon compared to one shown in Figure 5-7d. This result attests that the activity does correlate with the amount of the hydrophilic carboxyl group. The track of Mo 3d and W 4f electron through the course of activation in different potential window shows that only undergoing higher oxidizing potential would lead to oxidation of Mo and W to high valence states (Figure 5-14), which appears inevitable for producing the hydrophilic carboxyl group. Higher than 0.61 V, *e.g.* 0.8 V vs. RHE would lead to severe oxidation of the carbides, resulting in decreased performance as shown in Figure 5-15.

Figure 5 - 13 XPS of nw-W4Mo, C1s electron, after cyclic voltammetry activation from 0.26 V to 0.46 V vs. RHE in 0.5 M H₂SO₄

Figure 5 - 14 XPS of nw-W4MoC activated from 0.26 V to 0.61 V vs. RHE: (a) Mo 3d; (c) W 4f; nw-W4MoC activated from 0.26 V to 0.46 V: (b) Mo 3d; (d) W 4f.

Stability of nw-W4MoC is evaluated by cyclic voltammetry scan between -0.2 and 0.61 V vs. RHE, after which its polarization curves are recorded as shown in Figure 5-16. In comparison, the two polarization curves nearly overlap in low current region, and a slight decay at high current region is observed. Chronoamperometric electrolysis

Figure 5 - 15 polarization curve by cyclic voltammetry at different potential window, (a) 0.26 V to 0.61 V vs. RHE; (b) 0.26 V to 0.8 V vs. RHE in 0.5 M H₂SO₄.

also demonstrates a stable hydrogen evolution for ~ 20 h, indicating a good durability in acid. Moreover, we intentionally expose the freshly activated nw-W4MoC-electrode in air, and after 20 days, the polarization curve is taken in Figure 5-17. No severe performance deterioration was observed. This superior stability is ascribed to the carbon layer on the surface, which prevents further oxidation.

Figure 5 - 16 stability test of nw-W4MoC in 0.5 H₂SO₄ with an inset graph showing chronoamperometric electrolysis

Figure 5 - 17 polarization curve of freshly activated electrode and aged electrode

5.4. Conclusions

A bimetallic carbide consisting of Mo_2C and WC is realized in interwoven nanostructure. Nanosized Mo_2C is integrated onto WC nanowire through hydrothermal method, followed by a carburization route. The activated nw-W₄MoC featured in this interwoven structure is demonstrated as an outstanding catalyst to perform efficiently towards HER, in high current density at a fixed potential and high exchange current density, low onset potential and low charge transfer resistance. Emphasis is given on the modulation of surface property by CV techniques, which produces a hydrophilic interface between catalyst and electrolyte, and ensures this outstanding performance.

It is demonstrated that by incorporating a highly conductive support, *e.g.* WC and a good catalyst *e.g.* Mo_2C , excellent performance could be achieved. Besides, catalyst surface also plays an important role in heterogeneous catalytic reactions. New methodologies of quantifying the hydrophilicity is worthy to explore and needed in future, and it may guarantee improved performance.

Chapter 6 Molybdenum phosphide as an efficient electrocatalyst for hydrogen evolution reaction

(This chapter is reproduced from P. Xiao, M. Alam Sk, L. Thia, et al., *Molybdenum phosphide as an efficient electrocatalyst for hydrogen evolution reaction*. Energy & Environmental Science, 2014. 7(8): p. 2624-2629. With the permission of The Royal Society Chemistry)

6.1. Introduction

Hydrogen production through electrochemical water-splitting has been extensively pursued as it could potentially achieve a sustainable fuel production and the electricity required could be obtained from renewable energy [2]. Noble metals, *e.g.* Pt, demonstrate exceptional behavior with nearly zero overpotential in acidic media [293, 333, 334]. However, their high cost and scarcity impede their widespread usage and direct our attentions to earth-abundant metals or their compounds. Non-noble electrocatalysts can be categorized into two categories: (1) the derivatives of organic liganded metals (*e.g.* Ni, Mo, Fe), such as hydrogenases or metalloenzyme, the mimics of active site of hydrogenases [285, 335], molybdenum-oxo [335], pyrene-functionalized nickel complex [336]; (2) inorganic compounds of metals. MoS₂ [148, 151, 167, 174, 337], as a typical inorganic compound for hydrodesulfurization [338], was firstly discovered to possess biomimetic active sites as hydrogenases [125, 126]. Selenide [158, 159], nickel molybdenum nitride [287], carbide [190, 191, 193, 197], nickel phosphide [205, 212], and first-row of transitional metal dichalcogenides [320] are reported to be promising electrocatalysts towards hydrogen evolution reaction (HER). By comparison, those cost-effective catalysts as the potential substitutes for Pt are either functionalized by organic ligand, *e.g.* [NiFe]hydrogenase or inorganics *e.g.* MoS₂, Ni₂P,. In a typical ‘Volcano plot’ of hydrogen adsorption energy of common metals (M = Nb, Mo, Ni, Pt, Au, Ag etc.) [315, 339, 340], it is revealed that strong

metal-hydrogen (Mo, Ni etc.) bonds could impede hydrogen release from the active sites, compared to Pt group metals, *e.g.* Pd and Pt, which excludes those non-noble metals (*e.g.* Ni, Mo) as suitable candidates to catalyze hydrogen evolution reaction (HER). However, a subsequent study suggested that inorganic compounds of the non-noble metals can modify the metal-hydrogen bond strength and achieve a Pt-resembling Gibbs free energy for hydrogen evolution in acidic environment. The study of MoS₂ and Ni₂P has successfully underpinned this theoretical calculation[125, 198]. Inspired by this, herein, we report a molybdenum compound, MoP as a highly efficient catalyst for HER both in acidic and alkaline media. Molybdenum phosphide is synthesized through facile sintering of molybdenum and phosphorus precursor assisted by citric acid. Unlike MoS₂ which shows very poor activity in bulk form, MoP still exhibits high electrocatalytic activity in bulk form. Furthermore, it was also experimentally demonstrated that going from metal Mo, Mo₃P to MoP, different degrees of phosphorization results in distinct performances and different stability. Theoretically, we employed Density functional theory (DFT) calculation to elucidate underlying reasons behind the distinct performance by comparing the hydrogen chemisorption process and Gibbs free energy between Mo, Mo₃P and MoP.

6.2. Experimental

6.2.1 Materials synthesis and methods

Ammonium molybdate tetrahydrate, $((\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O})$, Sigma-Aldrich, Bioultra, >99.0%), Ammonium hydrogen phosphate $((\text{NH}_4)_2\text{HPO}_4)$, Sigma-Aldrich, reagent grade, $\geq 98.0\%$) and citric acid ($\text{C}_6\text{H}_8\text{O}_7$, Sigma-Aldrich, ACS reagent, $\geq 99.5\%$) are used as received and no further purification experiments are conducted. In a typical procedure, Stoichiometric $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$ (*i.e.* 1:1 for MoP and 3:1 Mo_3P in molar ratio) were dissolved in DI-water. Citric acid was added in a molar ratio of 2 (citric acid): 1 (Mo). After evaporation of water, the obtained brown slurry was dried, grinded and sintered at 500 °C for 5 h to prepare the precursor of catalyst. Catalysts MoP, Mo_3P can be synthesized in H_2 at 650, in Ar at 800 °C for 2 h, respectively. Note that the as-synthesized MoP and Mo_3P should be deactivated in 2 vol.% O_2/Ar for 2 h, after which they could be handled in ambient air. Metal Mo is obtained by reducing commercial MoO_3 by H_2 at elevated temperature (850 °C).

6.2.2 Materials characterization

Crystal structures of the as-synthesized Mo, Mo_3P and MoP were examined by an X-Ray diffraction (XRD) using a Cu $K\alpha$ radiation source (Bruker, D2 Phaser). For Morphology, a field emission scanning electron microscope (FE-SEM, JEOL, JSM6701F, Japan) coupled with Energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM, Philips CM300) were employed. To probe the composition, X-ray photoelectron spectroscopy (XPS) experiments were performed on a VG Escalab 200i-XL spectrometer equipped with a monochromatic Al $K\alpha$ (1486.6 eV) X-ray source.

6.2.3 Electrode preparation and electrochemical measurements

Polarization curves of the HER were collected by an Autolab PGSTAT302/FRA system (Eco Chemie, Netherland) in a three-electrode configuration at room

temperature, where Pt foil and Saturated Calomel Electrode (SCE) were used as the auxiliary electrode and the reference electrode, respectively. All the potentials were recorded with respect to the reversible hydrogen electrode (RHE). Catalyst ink was typically made by dispersing 7 mg of catalyst in 2 ml ethanol. After adding 0.5 ml of 0.05 wt.% of Nafion solution (Gashub, Singapore) and ultrasonication, an aliquot of 5 μL was pipetted onto the glassy carbon electrode (0.1963 cm^2) to reach the catalyst loading of 0.86 mg cm^{-2} . Current density was normalized to the geometrical area of the working electrode. Polarization data is collected at the scan rate of 2 mV/s on a rotation disk electrode under 2000 rpm. Especially, to circumvent the charge effect, the data for Tafel plot is collected under a staircase mode (with a step size of 5 mV). Electrochemical impedance spectroscopy (EIS) for the polarization of HER was carried out in a potentiostatic mode in the frequency range of 10^5 Hz to 0.01 Hz under the amplitude of 10 mV . At different overpotentials ($\eta=0 \sim 100\text{ mV}$), EIS curves were recorded.

6.2.4 Computational Methods and Models

All the calculation were performed using density-functional theory (DFT) method as implemented in a Vienna *ab initio* simulation package (VASP) [341-343] by using generalized gradient approximation Perdew-Burke-Eznerhof (GGA-PBE) method [344]. Projector augmented wave method (PAW) [345, 346] was used to describe the interaction between the atomic cores and electrons. Based on experimental data for bulk Mo ($a = b = c = 3.147\text{ \AA}$, space group: Im-3m) and MoP ($a = b = 3.231\text{ \AA}$, $c = 3.207\text{ \AA}$, $\gamma = 120^\circ$ and space group: P-6m2), we optimized all the structural parameters of bulk Mo and MoP by using $5 \times 5 \times 5$ Monkhorst-Pack k-point and an energy cut-off of 400 eV until the forces acting on each atom become less than $0.01\text{ eV/\AA}$. The calculated lattice parameters of Mo ($a = b = c = 3.152\text{ \AA}$) and MoP ($a = b = 3.229\text{ \AA}$)

and $c = 3.209 \text{ \AA}$) are in good agreement with experimental data. We adopted a catalytic model that is similar to a previous report [125] for Mo and MoP. The surfaces of Mo (110) and MoP (001) are chosen for the consideration of the dominating planes based on experimental observation. The 2×2 (110) Mo and (001) MoP surfaces were constructed by cleaving optimized bulk Mo and MoP in a six-atom-layer-thick slab. A $5 \times 5 \times 1$ Monkhorst-Pack k-point was employed accordingly. Since the cleaving of MoP will result in two different (001) surfaces, one with Mo as top surface (Mo-terminated) and other with P as top surface (P-terminated), we considered both the surfaces for the calculation.

6.2.4.1 Adsorption of H atom(s) on (110)-Mo and (001)-MoP surfaces

The differential adsorption energy of H adsorption is chosen to describe the stability of hydrogen according to the literature [125] and the equation is given below:

$$\Delta E_H = E(\text{MoP} + n\text{H}) - E(\text{MoP} + (n-1)\text{H}) - 1/2 E(\text{H}_2) \quad (1)$$

Where $E(\text{MoP} + n\text{H})$ is the total energy of MoP with the n hydrogen atoms adsorbed on surface, $E(\text{MoP} + (n-1)\text{H})$ is the total energy of MoP with $(n-1)$ hydrogen atoms adsorbed on surface and $E(\text{H}_2)$ is the total energy of hydrogen molecule in gas phase. The equation (1) gives the binding energy of single H atom adsorption when n is equal to (1). The calculated binding energy of single H atom on (110)-Mo and (001)-MoP, Mo terminated surface is listed in Table 6-1. The data shows that the 3-coordinated hollow site is preferable for H adsorption on (110)-Mo.

Table 6 - 1 Calculated binding energy (eV) of single H atom on (110)-Mo and (001)-MoP surfaces

Binding site	Binding energy (eV)	
	(110)-Mo	(001) MoP, Mo terminated
Top	-0.01	-0.11
Bridge	-0.63	- ^b
Hollow (H1) ^a	-0.77	-0.87
Hollow (H2) ^a	-0.77	-0.64

^a For definition see Figure 6-1, for (110)-Mo both the H1 and H2 site are same. ^b The adsorption on bridge site is unstable and the H atom moves to hollow site

Figure 6 - 1 Top view of (a) (110)-Mo and (b) (001)-MoP, Mo terminated surfaces; It shows the binding sites for H adsorption (only the first two atomic layers are shown. Mo – cyan sphere, P – magenta sphere).

For adsorption of H atom on (001)-MoP, Mo terminated surface we also consider top (T), bridge (B) and 3-coordinated hollow (see Figure 6-1a). The surface of (001)-MoP, Mo terminated surface has two hollow sites H1 and H2 (for definition see Figure 6-1b). The results show that H1 site is favorable for H adsorption. In contrast, for (001)-MoP, P terminated surface, the favorable binding site is the top side (see Figure 6-2).

Figure 6 - 2 Top view of H adsorbed (110)-Mo, (001)-MoP, Mo and P terminated surfaces. Only first two atomic layers are shown.

Based on the results of single H atom adsorption on the surface, we select the hollow site for adsorption of the second and more H atoms on (110)-Mo and (001)-MoP, Mo terminated surfaces while the top sites is chosen for (001)-MoP, P terminated surface.

The calculated differential binding energy of H atom on (110)-Mo, (001)-MoP, Mo terminated and (001)-MoP, P terminated surfaces is listed in Table 6-2. Since top surface of our surface models has four Mo or P atoms, adsorption of one, two, three and four H atom is considered as 1/4, 2/4, 3/4 and 4/4 monolayer (ML) coverage, respectively.

Table 6 - 2 Calculated binding energy and Gibbs free energy of H adsorption on (110) Mo and (001) MoP, Mo and P terminated surfaces

H Coverage	(110)-Mo		(001) MoP, Mo terminated		(001) MoP, P terminated	
	ΔE_H (eV)	ΔG_H° (eV)	ΔE_H (eV)	ΔG_H° (eV)	ΔE_H (eV)	ΔG_H° (eV)
1/4 ML	-0.77	-0.53	-0.87	-0.63	-0.64	-0.36
2/4 ML	-0.71	-0.47	-0.84	-0.60	-0.29	-0.03
3/4 ML	-0.70	-0.46	-0.82	-0.59	0.08	0.34
4/4 ML	-	-	-	-	0.28	0.54

6.2.4.2 Catalytic activity of Mo and MoP

To compare the catalytic activity of Mo and MoP, we calculated the Gibbs free energy of hydrogen adsorption following the equation below:

$$\Delta G_H^\circ = \Delta E_H + \Delta E_{ZPE} - T \Delta S_H \dots\dots\dots (2)$$

Where ΔE_{ZPE} is the difference in zero point energy between the adsorbed state and the gas phase, ΔS_H is the entropy difference between the adsorbed state and the gas phase. The gas phase entropy of H is taken from ref. [347]. The calculated ΔG_H° values for H adsorption on (110)-Mo, (001)-MoP, Mo and P terminated surfaces are listed in Table 6-2. It will be a good catalyst for hydrogen evolution if the free energy of adsorbed H is close to that of the reactant or product (*i.e.*, $\Delta G_H^\circ \cong 0$).

6.3. Results and Discussion

Mo_3P and MoP were synthesized at 800 °C and 650 °C respectively via a two-step sintering method (Experimental section, supporting information), whilst metal Mo was obtained by reducing MoO_3 in H_2 at 850 °C. Their corresponding XRD patterns are shown in Figure 6-3. The peaks are well indexed to the standard XRD profiles and no

Figure 6 - 3 XRD patterns of (a) Mo ; (b) Mo_3P ; (c) MoP .

major impurities are detected. Metal Mo , in a cubic pack (ICSD code: 643962) belongs to Im-3m (229). After incorporation phosphorus to form Mo_3P , it evolves to tetragonal structure. Its XRD pattern confirms its I-42m (121) in space group in Figure 6-3b, with Mo atom in either 2 or 4-coordinated by P atoms. Further phosphorization leads to MoP , in hexagonal structure (P-6m2), with Mo 6-coordinated by P atoms, as shown in Figure 6-3c. A more visualized structure change is presented in Figure 6-4.

Field-emission scanning electron microscopy (FE-SEM) and Transmission electron microscopy (TEM) were applied to examine its morphology. FE-SEM graphs in

Figure 6 - 4 schematic graph to show the structural evolution upon phosphorization

Figure 6 - 5 Morphology of MoP (a) FE-SEM and (b) TEM graph.

Figure 6-5a show that the as-synthesized MoP and Mo₃P (Figure 6-6) are in bulk form due to the calcination at high temperature. High-resolution TEM (HR-TEM) graph exhibits a well-arrayed (001) plane of MoP with the plane distance of 0.32 nm (Figure 6-5b), which is correlated with the peak at 28° by XRD characterization. Energy dispersive X-ray spectroscopy (EDS) results confirm the compositions of MoP and Mo₃P (Figure 6-7), which is quite consistent with the chemical formulas, 1:1 and 3:1 for MoP, Mo₃P respectively. To elucidate the valence states of individual elements of

Figure 6 - 6 bulk Mo₃P materials synthesized at 800 °C under Ar

Figure 6 - 7 EDS of as-synthesized (a) MoP and (b) Mo₃P. The calculated atomic ratios of Mo: P from EDS are 0.645/0.657 and 0.69/0.21.

MoP, X-ray photoelectron spectroscopy (XPS) experiments were conducted. Figure 6-8a and 6-8b show the XPS profile of Mo 3d and P 2p of the as-synthesized MoP. Deconvolution of the spectra indicates two doublets at 235.28 eV/232.08 eV (Mo⁺⁶ 3d_{3/2}/3d_{5/2}) and 231.9 eV/228.8 eV (Mo⁺⁴ 3d_{3/2}/3d_{5/2}) in Figure 6-8a, which can be assigned to high oxidation state of Mo (MoO₃ and MoO₂) [328, 329]. We believe that the oxidation only happens on the surface. To validate our hypothesis, we characterize the aged MoP (Figure 6-9) by XRD, which still manifests the well-crystallized MoP and does not indicate any discernible peaks of the oxides, implying a mere surface

Figure 6 - 8 X-ray photoelectron spectra (XPS) of the as-synthesized MoP (a) Mo 3d and (b) P 2p; aged MoP (c) Mo 3d and (d) P 2p.

Figure 6 - 9 XRD pattern of aged MoP

oxidation (less than 10 nm) that could only be detected by XPS. The rest of the XPS profile depicted in green (Figure 6-8a) is ascribed to MoP, represented by a 231.2 eV/228.0 eV doublet, which agrees well with previous report [200, 348]. The profile of P 2p also exhibits a peak with high binding energy (peak 1 in Figure 6-8b) which could be attributed to PO_4^{3-} or P_2O_5 [200] caused by oxidation. To identify the rest peaks for MoP, we further compared the XPS profile of the as-prepared MoP sample after test with the aged sample. As shown in Figure 6-8d, P 2p profile of the aged sample does not display the low-binding-energy peaks as we can observe in Figure 6-8b. On the contrary, it manifests even stronger peaks in the low-binding-energy region for the sample after test (Figure 6-10). Considering the above, we assign the doublet (130.1/129.2 eV for peak 2/peak 3) to low valence of P, MoP in this case.

Figure 6 - 10 MoP after electrochemical test (c) Mo 3d and (d) P 2p

In a three-electrode configuration, the catalytic activity towards HER was investigated in acid and alkaline media. Figure 6-11 shows the performance of Mo, Mo_3P and MoP in acidic medium; Pt/C was also tested as a comparison. Polarization curve and Tafel slope $\sim 30 \text{ mV dec}^{-1}$ of Pt/C presented in Figure 6-11a and 6-11b show consistency with previous studies [134]. Drop-casted on glassy carbon electrode (which exhibits

Figure 6 - 11 (a) Polarization curves of Mo, Mo₃P and MoP in 0.5 M H₂SO₄, scan rate: 2 mV s⁻¹; (b) Tafel plots in 0.5 M H₂SO₄; Electrochemical impedance spectra of MoP: (c) in 0.5 M H₂SO₄ and (d) in 1 M KOH.

negligible activity towards HER), to achieve the current density of 10 mA cm⁻², metal Mo requires the potential up to 0.5 V vs. RHE with the onset potential ~ 0.3 V vs. RHE, and Mo₃P is found to perform similarly as shown by the green line, indicating that metal Mo itself is not a good catalyst for HER and its phosphide Mo₃P is not suitable for HER either. In contrast, MoP shows a rather high performance in 0.5 M H₂SO₄. The onset of hydrogen evolution reaction can be observed at around 50 mV vs. RHE and the current density reaches 30 mA cm⁻² at the potential of 0.18 V vs. RHE. To clarify these differences in performance, in the perspective of elementary step, *i.e.* hydrogen chemisorption, we use Gibbs free energy (ΔG°_H) as the descriptor to assess the binding strength of catalysts to H (*e.g.* Mo and MoP) and evaluate the catalysts

(detailed DFT calculation can be found experimental section 6.2.4). Metal Mo exhibits a strong binding to H, indicated by highly negative binding energy (ΔE_H) in Table 6-1 when H coverage reaches 1/4 monolayer (ML, one hydrogen adsorbed on 2×2 slab). This agrees well with previous report [125]. Calculation of Mo terminated surface on (001)-MoP also shows a similar or even stronger binding to H which excludes Mo as the active site. Nevertheless, the investigation of P sites implies that P has played a crucial role by acting as a ‘hydrogen deliverer’. As shown in the Table S2, ΔG°_H changes from -0.36 eV to 0.54 eV when H coverage increases from 1/4 ML to full coverage, indicating that P could bond hydrogen at low coverage whilst desorb H at high coverage. This enables P to behave like a ‘hydrogen deliverer’, resembling the S-edges in MoS₂ [173]. Interestingly, when we applied the same method to calculate the binding energy of H on (001) of Mo₃P, where a four-P-site slab is chosen, the binding energy ΔE_H becomes positive (Table 6-3) with the initial two H adsorbed, indicating unfavorable binding of H on P site of Mo₃P. This is in accordance with experimental results.

Table 6 - 3 Calculated binding energy and Gibbs free energy of H adsorption on (001) Mo₃P, P terminated.

H Coverage	ΔE_H (eV)
1/4 ML	0.20
2/4 ML	0.14

As shown in Table 6-3 and the model below, where the top view of H adsorbed (001)- Mo_3P surface (only first two atomic layers are shown), and similar to MoP, the cleaving of Mo_3P will result in two different (001) surfaces, one with Mo as top surface (Mo-terminated) and other with P as top surface (P-terminated). As the (001) MoP, P-terminated surface is identified as the active sites for adsorption/desorption of H, we studied the H adsorption on (001) Mo_3P , P-terminated surface. The calculated binding energy of first and second H atom on (001) Mo_3P , P-terminated surface is 0.20 and 0.14 eV, respectively (see Table 6-3). The results indicate that the H adsorption on (001) Mo_3P , P-terminated surface is unfavorable, not rendering Mo_3P as a potential catalyst for HER.

After electrochemical testing, the catalyst composition was again examined by XPS. Compared to the as-synthesized MoP, XPS profile of the post-testing catalysts displays a similar profile to Mo 3d and P 2p shown in Figure 6-10 except for the decreased content of MoO_3 and MoO_2 . Previous study of Mo_2C by Hu et al. [190] has proved that MoO_3 and MoO_2 are not efficient catalysts, which further suggests the high performance could be attributed to MoP.

Tafel plots of Potential V - $\text{Log}|j(\text{current density})|$ could be interpreted by Volmer-Tafel or Heyrovsky mechanism in the classical two-electron-reaction model for cathodic HER [191]. The Tafel slope of 92 mV dec^{-1} (Figure 6-11b) for metal Mo suggests a typical Volmer-Tafel route with Volmer step as the rate-determining step. After phosphorization, it exhibits 147 mV dec^{-1} and 54 mV dec^{-1} for Mo_3P and MoP respectively. Here, the Tafel slope of 54 mV dec^{-1} implies that hydrogen evolution on MoP undergoes a Heyrovsky mechanism which is still different from the route those noble metals, *e.g.* Pt, are subjected to. Based on the Langmuir Isotherm model [330], a fast discharging reaction (Volmer reaction) rate under low coverage (< 0.1) of

adsorbed hydrogen (H_{ad}) leads to $\sim 30 \text{ mV dec}^{-1}$ and the Tafel slope of 54 mV dec^{-1} is most possibly caused by large coverage of H_{ad} (> 0.6). The large coverage of H is also rendered by theoretical calculation that zero ΔG°_H could be achieved at a certain coverage of H on P site from $2/4 \text{ ML}$ to $3/4 \text{ ML}$. In comparison with metal Mo, we can conclude that a simple phosphorization could completely change the reaction route. By extrapolating the Tafel plot to overpotential of 0 V , the exchange current density can be extracted (Table 6-4). It is found that MoP exhibits a value of $3.4 \times 10^{-2} \text{ mA cm}^{-2}$, ~ 70 times higher than that of metal Mo ($4.9 \times 10^{-4} \text{ mA cm}^{-2}$) and also outperforms MoS_2 that has been reported as a promising catalyst for HER [149, 158]. As a non-

Table 6 - 4 Tafel slope b and exchange current density j_0

	b (mV dec^{-1})	j_0 (mA cm^{-2})
Mo	92	4.9×10^{-4}
Mo₃P	147	--
MoP in 0.5 M H₂SO₄	54	3.4×10^{-2}
MoP in 1 M KOH	48	4.6×10^{-2}
Pt/C	33	0.63

noble catalyst in bulk form, MoP has achieved comparably competitive performance as Ni_2P [205], and is even superior to MoB, Mo_2C [190], $\text{Mo}_2\text{C}/\text{CNT}$ [191] at a similar loading for HER in acidic medium.

Few catalysts can exhibit good activity and stability under both acidic and alkaline conditions. *e.g.* Ni_2P was found to deteriorate rapidly in alkaline medium [205]. Herein we further examined the activity of MoP in both acidic and alkaline conditions using electrochemical impedance spectroscopy (EIS) technique. Bode plots of MoP (Figure 6-12) suggest a one-time-constant process in both acidic and alkaline media and Nyquist plots show a depressed arc intercepted by x-axis in Figure 6-11c and 6-11d. The high-frequency intersection with x-axis represents ohmic resistance, mainly

arising from the electrolyte and all contact resistances. To decouple the ohmic

Figure 6 - 12 Bode plot of MoP: (a) in 0.5 M H₂SO₄; (b) 1 M KOH

Table 6 - 5 Fitting data of EIS of MoP in 0.5 M H₂SO₄ and 1 M KOH

	R_s (Ω)	R_{ct} (Ω)	CPE	
			Q ($10^{-2} S s^n$)	n
0.5 M H₂SO₄ $\eta = 50$ mV	5.2	423.0	1.66	0.89
0.5 M H₂SO₄ $\eta = 100$ mV	6.0	40.0	1.31	0.86
1 M KOH $\eta = 50$ mV	5.4	195.0	0.80	0.89
1 M KOH $\eta = 100$ mV	5.1	30.9	0.90	0.78

resistance from polarization resistance, we applied a model of an ohmic resistance (R_s) in series with a module, where a polarization resistance (R_{ct}) is in parallel with a

constant phase element (CPE). As summarized in Table 6-5, MoP performs slightly better in alkaline medium than in acidic medium, indicated by smaller R_{ct} at the overpotential of 50 mV and 100 mV. Polarization curve in Figure 6-13a agrees with the EIS results. At low current density, MoP in alkaline medium outperforms that in acidic medium, and exhibits nearly overlapped polarization curve at high-current region, suggesting a good performance in alkaline medium.

Figure 6 - 13 (a) polarization curve before and after durability test, scan rate: 2 mV s⁻¹; (b) chronoamperometric electrolysis;

Durability is a key factor in evaluating catalyst performance. Long-term stability is investigated both in 1 M KOH and 0.5 M H₂SO₄. Unfortunately, slow corrosion happens in 1M KOH as shown in an amperometric plot (Figure 6-13b) and the performance degrades to ca. 60% of its initial value in 40 h (Figure 6-13a). However, chronoamperometric electrolysis evidences excellent stability of MoP in 0.5 M H₂SO₄ at applied potential of 0.14 mV vs. RHE in Figure 6-13b, and no performance degradation was observed after electrolysis for more than 40 h. Polarization curve after electrolysis shows slightly enhanced performance at the region of low current density, which could be ascribed to surface activation in cathodic polarization. In contrast, Mo and Mo₃P suffer from severe performance degradation under both acidic and alkaline

media. Inspection of morphology after stability test shows no difference compared to the one before test (Figure 6-14) in a panoramic view.

Figure 6 - 14 SEM graphs for before/after stability test

Mo is widely known as a chemically unstable metal in acidic media, and with insufficient phosphorization, the degradation of current density was observed even in the second scan of polarization curve of Mo_3P (not shown), implying that the corrosion occurs. Stability is commonly correlated with its structure. As shown in Figure 6-4, Mo atom is 6-coordinated by P atom in MoP in contrast to 2 or 4 P-atoms bonded in Mo_3P , which could probably be related to the stability in acidic or alkaline media, and suggest the significance of phosphorization.

6.4. Conclusions

Distinct performance was observed from traditional metal Mo phosphide compound. Our results show catalysts having a higher degree of phosphorization as in MoP results in better performance compared to lower degree of phosphorization or lack thereof as in Mo₃P and Mo respectively. Performance in this case is determined based on polarization, Tafel analysis in the low-current region, stability test by chronoamperometric electrolysis.

DFT calculation verified that the active site should be ascribed to P atoms, which achieves nearly zero Gibbs free energy. The results entitle P atom the role analogous to S atom in MoS₂, which is responsible to create numbers of edges for HER [126]. In summary, we have demonstrated that facile phosphorization can transform metal Mo, a poor catalyst, to MoP, an active and stable catalyst for HER. Similar to organic-ligand-functionalized metal, *e.g.* nickel complex [336], molybdenum-oxo [335], this strategy could be easily extended to other earth-abundant and inexpensive metals (*e.g.* Ni, Fe *etc.*).

Chapter 7 Conclusions and Perspectives

For hydrogen oxidation, we have verified the possibility of using SrMoO_3 as the electrical conductor to replace Ni, for the consideration of improving the sinterability, redox stability. As a potential candidate of anode for SOFC, the chemical compatibility of SrMoO_3 with YSZ, GDC has been examined, and demonstrated to be chemically compatible with them. Based on the composite backbone for anode, *i.e.* SrMoO_3 –YSZ, SrMoO_3 –GDC, catalytic activities are enhanced by wet-chemically infiltrating nano-sized GDC particles on SrMoO_3 –YSZ and calcium doping to substitute for Sr in SrMoO_3 –GDC. Improved performance is observed in both cases, which can be ascribed to the nano-sized GDC particles and ex-solved Mo particles as the catalysts, respectively. Overall, SrMoO_3 is a good anode material for SOFC with the attributes of being an excellent electrical conductor, in good compatibility with YSZ and GDC, achieving good redox stability. But SrMoO_3 lacks catalytic activity towards hydrogen oxidation. Metals ex-solution out of the host materials as the catalyst can be a good compensation if metal ex-solution can be realized in doped SrMoO_3 . In our work, calcium substituted SrMoO_3 has been demonstrated as a redox stable anode materials, with reversible metal Mo ex-solution/dissolution out of/in its host material, which results in improved performance. Activity is expected to be further enhanced if more active metal, *e.g.* Ni/Co/Ru/Pd, can be doped into SrMoO_3 with reversible ex-solution of metals in an individual or alloyed/hybrid form. Future work is warranted to examine the incorporation of these highly active metals, involving the investigation of ex-solving rate, and doping quantity. More importantly, redox stability is so critical that it needs to be confirmed. Through exploration of new synthetic routes, deliberate selection of the dopants with matched ionic size, we are

anticipating that Ni/Co/Ru/Pd doped SrMoO₃ not only keeps all the properties thereof, but also strengthens the catalytic activities for hydrogen oxidation.

For hydrogen production, literature review and our work have highlighted MoS₂, Mo₂C and phosphides as the earth-abundant non-noble catalysts. Among them, Mo₂C and phosphides seem to have exhibited advantageous performance over Mo₂S because of their intrinsic high conductivity. Besides, MoP and Mo₂C are found to be very active towards HER even in its bulk phase. This gives promise that nanostructured carbide/phosphides could render higher performance, which has been verified by our work – catalysing HER by porous Mo₂C and Mo₂C/WC nanowire. For phosphides, we have highlighted the significance of phosphorization by comparing the activity of Mo, Mo₃P and MoP – only the 6 coordinated Mo by P, *i.e.* MoP, gives a stable, high performance in catalysing HER. However, our synthetic route of MoP still results in bulk forms due to the sintering at 650 °C, which might underscore the performance of MoP. New synthetic routes have been explored for the realization of nanostructured phosphides, for example phosphorization can be realized below 350 °C *via* phosphite decomposition. Various nanostructures of nickel/cobalt phosphides are successfully synthesized, achieving excellent performance in acid. Its application to MoP needs to be confirmed in future work. High performance always compromises the stability. Here, highly active carbide and phosphides towards HER originates from the active sites – the highly active surface. Surface oxidation of carbide and phosphides happen when exposed to air, and inevitably diminish the active sites, *e.g.* PO₄³⁻ for P oxidation in MoP on the surface. The strategy of preparation of carbide and phosphide with highly active surface and suppression of the surface oxidation will be the central focus in future work, and is crucial for the advancement of earth-abundant non-noble catalysts to deliver hydrogen in a high efficient, more reliable way.

References

1. Smith, B.H. and M.D. Gross, *A Highly Conductive Oxide Anode for Solid Oxide Fuel Cells*. Electrochemical and Solid-State Letters, 2011. **14**(1): p. B1-B5.
2. Turner, J.A., *Sustainable Hydrogen Production*. Science, 2004. **305**(5686): p. 972-974.
3. Jone, L.W., *Toward a liquid hydrogen fuel economy*. 1970, University of Michigan Environmental Action for Survival Teach In. Ann Arbor, Michigan: Michigan.
4. Pudukudy, M., et al., *Renewable hydrogen economy in Asia – Opportunities and challenges: An overview*. Renewable and Sustainable Energy Reviews, 2014. **30**(0): p. 743-757.
5. Marbán, G. and T. Valdés-Solís, *Towards the hydrogen economy?* International Journal of Hydrogen Energy, 2007. **32**(12): p. 1625-1637.
6. Farrauto, R.J., *New catalysts and reactor designs for the hydrogen economy*. Chemical Engineering Journal, 2014. **238**(0): p. 172-177.
7. Crabtree, G.W., M.S. Dresselhaus, and M.V. Buchanan, *The hydrogen economy*. Print edition, 2004. **57**(12): p. 39-44.
8. Murray, L.J., M. Dinca, and J.R. Long, *Hydrogen storage in metal-organic frameworks*. Chemical Society Reviews, 2009. **38**(5): p. 1294-1314.
9. Sakintuna, B., F. Lamari-Darkrim, and M. Hirscher, *Metal hydride materials for solid hydrogen storage: A review*. International Journal of Hydrogen Energy, 2007. **32**(9): p. 1121-1140.
10. Liu, C., et al., *Hydrogen Storage in Single-Walled Carbon Nanotubes at Room Temperature*. Science, 1999. **286**(5442): p. 1127-1129.
11. Armor, J.N., *Catalysis and the hydrogen economy*. Catalysis Letters, 2005. **101**(3-4): p. 131-135.
12. Kandemir, T., et al., *The Haber–Bosch Process Revisited: On the Real Structure and Stability of “Ammonia Iron” under Working Conditions*. Angewandte Chemie International Edition, 2013. **52**(48): p. 12723-12726.
13. Das, L.M., *Hydrogen engines: A view of the past and a look into the future*. International Journal of Hydrogen Energy, 1990. **15**(6): p. 425-443.
14. Verhelst, S. and T. Wallner, *Hydrogen-fueled internal combustion engines*. Progress in Energy and Combustion Science, 2009. **35**(6): p. 490-527.
15. Nieminen, J. and I. Dincer, *Comparative exergy analyses of gasoline and hydrogen fuelled ICEs*. International Journal of Hydrogen Energy, 2010. **35**(10): p. 5124-5132.
16. Sáinz, D., et al., *Conversion of a commercial gasoline vehicle to run bi-fuel (hydrogen-gasoline)*. International Journal of Hydrogen Energy, 2012. **37**(2): p. 1781-1789.
17. Huyskens, P., et al., *The technical implementation of a retrofit hydrogen PFI system on a passenger car*. 2011, SAE Technical Paper.
18. Verhelst, S., *Recent progress in the use of hydrogen as a fuel for internal combustion engines*. International Journal of Hydrogen Energy, 2014. **39**(2): p. 1071-1085.
19. White, C.M., R.R. Steeper, and A.E. Lutz, *The hydrogen-fueled internal combustion engine: a technical review*. International Journal of Hydrogen Energy, 2006. **31**(10): p. 1292-1305.
20. Furuhashi, S., M. Hiruma, and Y. Enomoto, *Development of a liquid hydrogen car*. International Journal of Hydrogen Energy, 1978. **3**(1): p. 61-81.
21. Tang, X., et al., *Ford P2000 hydrogen engine dynamometer development*. 2002, SAE Technical Paper.
22. Grimes, P. *Historical pathways for fuel cells. The new electric century*. in *Battery Conference on Applications and Advances, 2000. The Fifteenth Annual*. 2000.
23. Andújar, J.M. and F. Segura, *Fuel cells: History and updating. A walk along two centuries*. Renewable and Sustainable Energy Reviews, 2009. **13**(9): p. 2309-2322.

24. Merle, G., M. Wessling, and K. Nijmeijer, *Anion exchange membranes for alkaline fuel cells: A review*. Journal of Membrane Science, 2011. **377**(1–2): p. 1-35.
25. McLean, G.F., et al., *An assessment of alkaline fuel cell technology*. International Journal of Hydrogen Energy, 2002. **27**(5): p. 507-526.
26. Ellis, M.W., M.R. Von Spakovsky, and D.J. Nelson, *Fuel cell systems: efficient, flexible energy conversion for the 21st century*. Proceedings of the IEEE, 2001. **89**(12): p. 1808-1818.
27. Bing, Y., et al., *Nanostructured Pt-alloy electrocatalysts for PEM fuel cell oxygen reduction reaction*. Chemical Society Reviews, 2010. **39**(6): p. 2184-2202.
28. Beard, B.C. and P.N. Ross, *The Structure and Activity of Pt - Co Alloys as Oxygen Reduction Electrocatalysts*. Journal of The Electrochemical Society, 1990. **137**(11): p. 3368-3374.
29. Li, X., et al., *Development of Method for Synthesis of Pt – Co Cathode Catalysts for PEM Fuel Cells*. Electrochemical and Solid-State Letters, 2007. **10**(11): p. B201-B205.
30. Colón-Mercado, H.R., H. Kim, and B.N. Popov, *Durability study of Pt3Ni1 catalysts as cathode in PEM fuel cells*. Electrochemistry Communications, 2004. **6**(8): p. 795-799.
31. Yano, H., et al., *Oxygen Reduction Activity of Carbon-Supported Pt–M (M = V, Ni, Cr, Co, and Fe) Alloys Prepared by Nanocapsule Method*. Langmuir, 2007. **23**(11): p. 6438-6445.
32. Duan, H., Q. Hao, and C. Xu, *Nanoporous PtFe alloys as highly active and durable electrocatalysts for oxygen reduction reaction*. Journal of Power Sources, 2014. **269**(0): p. 589-596.
33. Rubinov, E., et al., *Insight into the formation mechanism of PtCu alloy nanoparticles*. CrystEngComm, 2014.
34. Zhu, C.-M., et al., *Pt-Cu Bimetallic Electrocatalysts with Enhanced Catalytic Properties for Oxygen Reduction*. Chemical Communications, 2014.
35. Vishnyakov, V.M., *Proton exchange membrane fuel cells*. Vacuum, 2006. **80**(10): p. 1053-1065.
36. Bagotsky, V.S., *Phosphoric Acid Fuel Cells*, in *Fuel Cells*. 2012, John Wiley & Sons, Inc. p. 99-106.
37. Paffett, M.T., et al., *The physical and chemical state of phosphoric acid fuel cell assemblies after long term operation: surface and near-surface analysis*. Journal of Power Sources, 1991. **36**(2): p. 137-153.
38. Raney, M., *Method of producing finely-divided nickel*. 1927: US patent.
39. Raney, M., *Method of preparing catalytic material*. 1925: US patent.
40. Gülzow, E., *Alkaline fuel cells: a critical view*. Journal of Power Sources, 1996. **61**(1–2): p. 99-104.
41. Wilson, B.P., et al., *Life cycle assessment of gas atomised sponge nickel for use in alkaline hydrogen fuel cell applications*. Journal of Power Sources, 2013. **243**(0): p. 242-252.
42. Fan, C., D.L. Piron, and M. Rojas, *Polarization of cobalt-molybdenum and nickel-molybdenum hydrogen electrodes for alkaline fuel cells*. International Journal of Hydrogen Energy, 1994. **19**(1): p. 29-33.
43. Mund, K., G. Richter, and F. von Sturm, *Titanium - Containing Raney Nickel Catalyst for Hydrogen Electrodes in Alkaline Fuel Cell Systems*. Journal of The Electrochemical Society, 1977. **124**(1): p. 1-6.
44. Kenjo, T., *Chromium - Doped Raney Nickel Catalyst for Hydrogen Electrodes in Alkaline Fuel Cells*. Journal of The Electrochemical Society, 1985. **132**(2): p. 383-386.
45. Jenseit, W., A. Khalil, and H. Wendt, *Material properties and processing in the production of fuel cell components: I. Hydrogen anodes from Raney nickel for*

- lightweight alkaline fuel cells*. Journal of Applied Electrochemistry, 1990. **20**(6): p. 893-900.
46. Al-Saleh, M.A., et al., *Steady state performance of copper impregnated Ni/PTFE gas diffusion electrode in alkaline fuel cell*. International Journal of Hydrogen Energy, 1996. **21**(8): p. 657-661.
 47. Raj, I.A. and K.I. Vasu, *Transition metal-based cathodes for hydrogen evolution in alkaline solution: Electrocatalysis on nickel-based ternary electrolytic codeposits*. Journal of Applied Electrochemistry, 1992. **22**(5): p. 471-477.
 48. Sheng, W., et al., *Non-precious metal electrocatalysts with high activity for hydrogen oxidation reaction in alkaline electrolytes*. Energy & Environmental Science, 2014. **7**(5): p. 1719-1724.
 49. Lee, H.-K., et al., *Oxygen reduction behavior with silver alloy catalyst in alkaline media*. Materials Chemistry and Physics, 1996. **45**(3): p. 238-242.
 50. Mogensen, D., et al., *Internal steam reforming in solid oxide fuel cells: Status and opportunities of kinetic studies and their impact on modelling*. Journal of Power Sources, 2010. **196**(1): p. 25-38.
 51. Liu, J. and S.A. Barnett, *Operation of anode-supported solid oxide fuel cells on methane and natural gas*. Solid State Ionics, 2003. **158**(1-2): p. 11-16.
 52. Lin, Y., et al., *Direct operation of solid oxide fuel cells with methane fuel*. Solid State Ionics, 2005. **176**(23-24): p. 1827-1835.
 53. Chen, Y., et al., *Novel functionally graded acicular electrode for solid oxide cells fabricated by the freeze-tape-casting process*. Journal of Power Sources, 2012. **213**(0): p. 93-99.
 54. Colson, C.M. and M.H. Nehrir, *Evaluating the Benefits of a Hybrid Solid Oxide Fuel Cell Combined Heat and Power Plant for Energy Sustainability and Emissions Avoidance*. Energy Conversion, IEEE Transactions on, 2011. **26**(1): p. 140-148.
 55. *The Bloom Box: A Solid Oxide Fuel Cell*. In 2010, after a '60 min' segment on the Bloom Box fuel cell aired on CBS, City Light commissioned the Wenatchi Group, Inc. to undertake a brief review of its applicability in City Light's service area.
 56. Waldbillig, D., A. Wood, and D.G. Ivey, *Thermal analysis of the cyclic reduction and oxidation behaviour of SOFC anodes*. Solid State Ionics, 2005. **176**(9-10): p. 847-859.
 57. Huang, Y.-H., et al., *Double Perovskites as Anode Materials for Solid-Oxide Fuel Cells*. Science, 2006. **312**(5771): p. 254-257.
 58. US Energy Information Administration. *The impact of increased use of Hydrogen on petroleum consumption and carbon dioxide emission (US Energy Information Administration, 2008.)*.
 59. Boyano, A., et al., *Exergoenvironmental analysis of a steam methane reforming process for hydrogen production*. Energy, 2011. **36**(4): p. 2202-2214.
 60. Zhou, G., et al., *High Activity of Ce_{1-x}Ni_xO_{2-y} for H₂ Production through Ethanol Steam Reforming: Tuning Catalytic Performance through Metal-Oxide Interactions*. Angewandte Chemie, 2010. **122**(50): p. 9874-9878.
 61. Nichele, V., et al., *Glycerol steam reforming for hydrogen production: Design of Ni supported catalysts*. Applied Catalysis B: Environmental, 2012. **111-112**(0): p. 225-232.
 62. Das, D. and T.N. Veziroğlu, *Hydrogen production by biological processes: a survey of literature*. International Journal of Hydrogen Energy, 2001. **26**(1): p. 13-28.
 63. Argun, H. and F. Kargi, *Bio-hydrogen production by different operational modes of dark and photo-fermentation: An overview*. International Journal of Hydrogen Energy, 2011. **36**(13): p. 7443-7459.

64. Winkler, M., et al., *[Fe]-hydrogenases in green algae: photo-fermentation and hydrogen evolution under sulfur deprivation*. International Journal of Hydrogen Energy, 2002. **27**(11–12): p. 1431-1439.
65. Melis, A., et al., *Sustained Photobiological Hydrogen Gas Production upon Reversible Inactivation of Oxygen Evolution in the Green Alga *Chlamydomonas reinhardtii**. Plant Physiology, 2000. **122**(1): p. 127-136.
66. Levin, D.B. and R. Chahine, *Challenges for renewable hydrogen production from biomass*. International Journal of Hydrogen Energy, 2010. **35**(10): p. 4962-4969.
67. Baykara, S.Z., *Hydrogen production by direct solar thermal decomposition of water, possibilities for improvement of process efficiency*. International Journal of Hydrogen Energy, 2004. **29**(14): p. 1451-1458.
68. Wang, Z., et al., *Comparison of thermochemical, electrolytic, photoelectrolytic and photochemical solar-to-hydrogen production technologies*. International Journal of Hydrogen Energy, 2012. **37**(21): p. 16287-16301.
69. Anzieu, P., et al., *The sulphur–iodine and other thermochemical process studies at CEA*. International journal of nuclear hydrogen production and application, 2010. **Vol.1**(No.2): p. 144-53.
70. Guo, H., et al., *Simulation Study on the Distillation of Hyper-Pseudoazeotropic HI–I₂–H₂O Mixture*. Industrial & Engineering Chemistry Research, 2011. **50**(20): p. 11644-11656.
71. Frank, S.N. and A.J. Bard, *Heterogeneous photocatalytic oxidation of cyanide and sulfite in aqueous solutions at semiconductor powders*. The Journal of Physical Chemistry, 1977. **81**(15): p. 1484-1488.
72. Yang, H.G., et al., *Solvothermal Synthesis and Photoreactivity of Anatase TiO₂ Nanosheets with Dominant {001} Facets*. Journal of the American Chemical Society, 2009. **131**(11): p. 4078-4083.
73. Liu, G., et al., *Nanosized anatase TiO₂ single crystals for enhanced photocatalytic activity*. Chemical Communications, 2010. **46**(5): p. 755-757.
74. Domen, K., et al., *Novel photocatalysts, ion-exchanged K₄Nb₆O₁₇, with a layer structure*. Journal of the Chemical Society, Chemical Communications, 1986(23): p. 1706-1707.
75. Kato, H., K. Asakura, and A. Kudo, *Highly Efficient Water Splitting into H₂ and O₂ over Lanthanum-Doped NaTaO₃ Photocatalysts with High Crystallinity and Surface Nanostructure*. Journal of the American Chemical Society, 2003. **125**(10): p. 3082-3089.
76. Maeda, K., et al., *GaN:ZnO Solid Solution as a Photocatalyst for Visible-Light-Driven Overall Water Splitting*. Journal of the American Chemical Society, 2005. **127**(23): p. 8286-8287.
77. Sato, J., et al., *RuO₂-Loaded β-Ge₃N₄ as a Non-Oxide Photocatalyst for Overall Water Splitting*. Journal of the American Chemical Society, 2005. **127**(12): p. 4150-4151.
78. Goldsmith, J.I., et al., *Discovery and High-Throughput Screening of Heteroleptic Iridium Complexes for Photoinduced Hydrogen Production*. Journal of the American Chemical Society, 2005. **127**(20): p. 7502-7510.
79. Rau, S., et al., *A Supramolecular Photocatalyst for the Production of Hydrogen and the Selective Hydrogenation of Toluene*. Angewandte Chemie International Edition, 2006. **45**(37): p. 6215-6218.
80. Ursua, A., L.M. Gandia, and P. Sanchis, *Hydrogen Production From Water Electrolysis: Current Status and Future Trends*. Proceedings of the IEEE, 2012. **100**(2): p. 410-426.
81. Carmo, M., et al., *A comprehensive review on PEM water electrolysis*. International Journal of Hydrogen Energy, 2013. **38**(12): p. 4901-4934.

82. Dusastre, V. and J.A. Kilner, *Optimisation of composite cathodes for intermediate temperature SOFC applications*. Solid State Ionics, 1999. **126**(1–2): p. 163-174.
83. Abernathy, H., et al., *Reversible aging behavior of La_{0.8}Sr_{0.2}MnO₃ electrodes at open circuit*. Journal of Power Sources, 2012. **216**(0): p. 11-14.
84. Dixon, E., J. Hadermann, and M.A. Hayward, *Structures and Magnetism of La_{1-x}Sr_xMnO₃ – (0.5+x)/2 (0.67 ≤ x ≤ 1) Phases*. Chemistry of Materials, 2012.
85. Fearn, S., et al., *Measurement of oxygen transport in La_{0.8}Sr_{0.2}MnO₃ perovskite grains*. Solid State Ionics, 2012(0).
86. Sayagués, M.J., J.M. Córdoba, and F.J. Gotor, *Room temperature mechanosynthesis of the La_{1-x}Sr_xMnO_{3±δ} (0 ≤ x ≤ 1) system and microstructural study*. Journal of Solid State Chemistry, 2012(0).
87. Grande, T., J.R. Tolchard, and S.M. Selbach, *Anisotropic Thermal and Chemical Expansion in Sr-Substituted LaMnO_{3+δ}: Implications for Chemical Strain Relaxation*. Chemistry of Materials, 2011.
88. Siqueira, G.O., et al., *Determination of the Mn³⁺/Mn⁴⁺ ratio in La_{1-x}Sr_xMnO_{3±d} powders*. Journal of Alloys and Compounds, 2012(0).
89. Jiang, S., *Development of lanthanum strontium manganite perovskite cathode materials of solid oxide fuel cells: a review*. Journal of Materials Science, 2008. **43**(21): p. 6799-6833.
90. Ianoş, R., et al., *Comparative study regarding the formation of La_{1-x}Sr_xCrO₃ perovskite using unconventional synthesis methods*. Journal of Thermal Analysis and Calorimetry, 2008. **94**(2): p. 343-348.
91. Brylewski, T., et al., *Screen-printed (La,Sr)CrO₃ coatings on ferritic stainless steel interconnects for solid oxide fuel cells using nanopowders prepared by means of ultrasonic spray pyrolysis*. Journal of Power Sources, 2012. **208**(0): p. 86-95.
92. Tao, S. and J.T.S. Irvine, *A redox-stable efficient anode for solid-oxide fuel cells*. Nature Materials, 2003. **2**(5): p. 320-323.
93. Huang, B., et al., *Performance of La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-δ} perovskite-structure anode material at lanthanum gallate electrolyte for IT-SOFC running on ethanol fuel*. Journal of Power Sources, 2007. **167**(1): p. 39-46.
94. Gross, M.D., J.M. Vohs, and R.J. Gorte, *An Examination of SOFC Anode Functional Layers Based on Ceria in YSZ*. Journal of the Electrochemical Society, 2007. **154**(7): p. B694-B699.
95. Jiang, S.P. and Y. Ye, *Pd-promoted La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O₃/YSZ Composite Anodes for Solid Oxide Fuel Cells*. ECS Transactions, 2008. **13**(26): p. 145-152.
96. Abudula, A., et al., *Oxidation mechanism and effective anode thickness of SOFC for dry methane fuel*. Solid State Ionics, 1996. **86–88, Part 2**(0): p. 1203-1209.
97. Kim, G., et al., *Investigation of the Structural and Catalytic Requirements for High-Performance SOFC Anodes Formed by Infiltration of LSCM*. Electrochemical and Solid-State Letters, 2009. **12**(3): p. B48-B52.
98. Kim, G., et al., *Engineering Composite Oxide SOFC Anodes for Efficient Oxidation of Methane*. Electrochemical and Solid-State Letters, 2008. **11**(2): p. B16-B19.
99. Rath, M.K., B.-H. Choi, and K.-T. Lee, *Properties and electrochemical performance of La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-δ}–La_{0.2}Ce_{0.8}O_{2-δ} composite anodes for solid oxide fuel cells*. Journal of Power Sources, 2012. **213**(0): p. 55-62.
100. Ding, H., J. Ge, and X. Xue, *A Ceramic-Anode Supported Low Temperature Solid Oxide Fuel Cell*. Electrochemical and Solid-State Letters, 2012. **15**(6): p. B86-B89.
101. van den Bossche, M. and S. McIntosh, *Pulse Reactor Studies to Assess the Potential of La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.4}X_{0.1}O_{3-δ} (X = Co, Fe, Mn, Ni, V) as Direct Hydrocarbon Solid Oxide Fuel Cell Anodes*. Chemistry of Materials, 2010. **22**(21): p. 5856-5865.

102. Kobsiriphat, W., et al., *La_{0.8}Sr_{0.2}Cr_{1-x}Ru_xO_{3-δ}-Gd_{0.1}Ce_{0.9}O_{1.95} solid oxide fuel cell anodes: Ru precipitation and electrochemical performance*. Solid State Ionics, 2009. **180**(2-3): p. 257-264.
103. Lay, E., G. Gauthier, and L. Dessemond, *Preliminary studies of the new Ce-doped La/Sr chromo-manganite series as potential SOFC anode or SOEC cathode materials*. Solid State Ionics, 2011. **189**(1): p. 91-99.
104. Lay, E., et al., *Ce-substituted LSCM as new anode material for SOFC operating in dry methane*. Solid State Ionics, 2008. **179**(27-32): p. 1562-1566.
105. Jardiel, T., et al., *New SOFC electrode materials: The Ni-substituted LSCM-based compounds (La_{0.75}Sr_{0.25})(Cr_{0.5}Mn_{0.5-x}Ni_x)O_{3-δ} and (La_{0.75}Sr_{0.25})(Cr_{0.5-x}Ni_xMn_{0.5})O_{3-δ}*. Solid State Ionics, 2010. **181**(19-20): p. 894-901.
106. Adjianto, L., et al., *Transition metal-doped rare earth vanadates: a regenerable catalytic material for SOFC anodes*. Journal of Materials Chemistry, 2012. **22**(22): p. 11396-11402.
107. Vasala, S., et al., *Isovalent and aliovalent substitution effects on redox chemistry of Sr₂MgMoO_{6-δ} SOFC-anode material*. Solid State Ionics, 2010. **181**(15-16): p. 754-759.
108. Zhang, L., et al., *Double-perovskites A₂FeMoO_{6-δ} (A=Ca, Sr, Ba) as anodes for solid oxide fuel cells*. Journal of Power Sources, 2010. **195**(19): p. 6356-6366.
109. Wang, Z., Y. Tian, and Y. Li, *Direct CH₄ fuel cell using Sr₂FeMoO₆ as an anode material*. Journal of Power Sources, 2011. **196**(15): p. 6104-6109.
110. Rager, J., et al., *Oxygen Stoichiometry in Sr₂FeMoO₆, the Determination of Fe and Mo Valence States, and the Chemical Phase Diagram of SrO-Fe₃O₄-MoO₃*. Journal of the American Ceramic Society, 2004. **87**(7): p. 1330-1335.
111. Liu, Q., et al., *A Novel Electrode Material for Symmetrical SOFCs*. Advanced Materials, 2010. **22**(48): p. 5478-5482.
112. Liu, Q., et al., *Sr₂Fe_{1.5}Mo_{0.5}O_{6-δ} as a regenerative anode for solid oxide fuel cells*. Journal of Power Sources, 2011. **196**(22): p. 9148-9153.
113. Li, X., et al., *La and Sc co-doped SrTiO₃ as novel anode materials for solid oxide fuel cells*. Electrochemistry Communications, 2008. **10**(10): p. 1567-1570.
114. Fu, Q., et al., *An efficient ceramic-based anode for solid oxide fuel cells*. Journal of Power Sources, 2007. **171**(2): p. 663-669.
115. Vasala, S., et al., *Degree of order and redox balance in B-site ordered double-perovskite oxides, Sr₂MMoO_{6-δ} (M=Mg, Mn, Fe, Co, Ni, Zn)*. Journal of Solid State Chemistry, 2010. **183**(5): p. 1007-1012.
116. Ji, Y., et al., *Electrochemical performance of La-doped Sr₂MgMoO_{6-δ} in natural gas*. Electrochemistry Communications, 2007. **9**(8): p. 1881-1885.
117. Xie, Z., et al., *Synthesis and electrical properties of Al-doped Sr₂MgMoO_{6-δ} as an anode material for solid oxide fuel cells*. International Journal of Hydrogen Energy, 2011. **36**(12): p. 7257-7264.
118. Wei, T., et al., *Cobalt-based double-perovskite symmetrical electrodes with low thermal expansion for solid oxide fuel cells*. Journal of Materials Chemistry, 2012. **22**(1): p. 225-231.
119. Huang, Y.-H., et al., *Double-Perovskite Anode Materials Sr₂MMoO₆ (M = Co, Ni) for Solid Oxide Fuel Cells*. Chemistry of Materials, 2009. **21**(11): p. 2319-2326.
120. Marrero-López, D., et al., *High temperature phase transition in SOFC anodes based on Sr₂MgMoO_{6-δ}*. Journal of Solid State Chemistry, 2009. **182**(5): p. 1027-1034.
121. Zhang, L. and T. He, *Performance of double-perovskite Sr_{2-x}Sm_xMgMoO_{6-δ} as solid-oxide fuel-cell anodes*. Journal of Power Sources, 2011. **196**(20): p. 8352-8359.

122. He, B., et al., *Sr₂Fe_{1.5}Mo_{0.5}O_{6-δ}-Sm_{0.2}Ce_{0.8}O_{1.9} Composite Anodes for Intermediate-Temperature Solid Oxide Fuel Cells*. Journal of the Electrochemical Society, 2012. **159**(5): p. B619-B626.
123. Zhang, L., et al., *Enhancement in surface exchange coefficient and electrochemical performance of Sr₂Fe_{1.5}Mo_{0.5}O₆ electrodes by Ce_{0.8}Sm_{0.2}O_{1.9} nanoparticles*. Electrochemistry Communications, 2011. **13**(7): p. 711-713.
124. Dai, N., et al., *One-step synthesis of high performance Sr₂Fe_{1.5}Mo_{0.5}O₆-Sm_{0.2}Ce_{0.8}O_{1.9} composite cathode for intermediate-temperature solid oxide fuel cells using a self-combustion technique*. Journal of Power Sources, 2012. **217**(0): p. 519-523.
125. Hinnemann, B., et al., *Biomimetic Hydrogen Evolution: MoS₂ Nanoparticles as Catalyst for Hydrogen Evolution*. Journal of the American Chemical Society, 2005. **127**(15): p. 5308-5309.
126. Jaramillo, T.F., et al., *Identification of Active Edge Sites for Electrochemical H₂ Evolution from MoS₂ Nanocatalysts*. Science, 2007. **317**(5834): p. 100-102.
127. Late, D.J., et al., *Hysteresis in Single-Layer MoS₂ Field Effect Transistors*. ACS Nano, 2012. **6**(6): p. 5635-5641.
128. Lukowski, M.A., et al., *Enhanced Hydrogen Evolution Catalysis from Chemically Exfoliated Metallic MoS₂ Nanosheets*. Journal of the American Chemical Society, 2013. **135**(28): p. 10274-10277.
129. Jin, S., et al., *Highly Active Hydrogen Evolution Catalysis from Metallic WS₂ Nanosheets*. Energy & Environmental Science, 2014.
130. Eda, G., et al., *Coherent Atomic and Electronic Heterostructures of Single-Layer MoS₂*. ACS Nano, 2012. **6**(8): p. 7311-7317.
131. Voiry, D., et al., *Conducting MoS₂ Nanosheets as Catalysts for Hydrogen Evolution Reaction*. Nano Letters, 2013. **13**(12): p. 6222-6227.
132. Bissessur, R., et al., *Encapsulation of polymers into MoS₂ and metal to insulator transition in metastable MoS₂*. Journal of the Chemical Society, Chemical Communications, 1993(20): p. 1582-1585.
133. Jiménez Sandoval, S., et al., *Raman study and lattice dynamics of single molecular layers of MoS₂*. Physical Review B, 1991. **44**(8): p. 3955-3962.
134. Li, Y., et al., *MoS₂ Nanoparticles Grown on Graphene: An Advanced Catalyst for the Hydrogen Evolution Reaction*. Journal of the American Chemical Society, 2011. **133**(19): p. 7296-7299.
135. Chang, K. and W. Chen, *In situ synthesis of MoS₂/graphene nanosheet composites with extraordinarily high electrochemical performance for lithium ion batteries*. Chemical Communications, 2011. **47**(14): p. 4252-4254.
136. Firmiano, E.G.S., et al., *Graphene oxide as a highly selective substrate to synthesize a layered MoS₂ hybrid electrocatalyst*. Chemical Communications, 2012. **48**(62): p. 7687-7689.
137. Chang, Y.-H., et al., *Three-Dimensional Molybdenum Sulfide Sponges for Electrocatalytic Water Splitting*. Small, 2013: p. n/a-n/a.
138. Wang, T., et al., *Enhanced Electrocatalytic Activity for Hydrogen Evolution Reaction from Self-Assembled Monodispersed Molybdenum Sulfides nanoparticles on an Au electrode*. Energy & Environmental Science, 2012.
139. Smith, A.J., et al., *Molybdenum Sulfide Supported on Crumpled Graphene Balls for Electrocatalytic Hydrogen Production*. Advanced Energy Materials, 2014: p. n/a-n/a.
140. Liao, L., et al., *MoS₂ Formed on Mesoporous Graphene as a Highly Active Catalyst for Hydrogen Evolution*. Advanced Functional Materials, 2013: p. n/a-n/a.

141. Yan, Y., et al., *Nano-tungsten carbide decorated graphene as co-catalysts for enhanced hydrogen evolution on molybdenum disulfide*. Chemical Communications, 2013. **49**(43): p. 4884-4886.
142. Chang, Y.-H., et al., *Highly Efficient Electrocatalytic Hydrogen Production by MoS_x Grown on Graphene-Protected 3D Ni Foams*. Advanced Materials, 2013. **25**(5): p. 756-760.
143. Yang, J., et al., *Two-Dimensional Hybrid Nanosheets of Tungsten Disulfide and Reduced Graphene Oxide as Catalysts for Enhanced Hydrogen Evolution*. Angewandte Chemie International Edition, 2013: p. n/a-n/a.
144. Yan, Y., et al., *Facile synthesis of low crystalline MoS₂ nanosheet-coated CNTs for enhanced hydrogen evolution reaction*. Nanoscale, 2013. **5**(17): p. 7768-7771.
145. Lin, T.-W., C.-J. Liu, and J.-Y. Lin, *Facile synthesis of MoS₃/carbon nanotube nanocomposite with high catalytic activity toward hydrogen evolution reaction*. Applied Catalysis B: Environmental, 2013. **134–135**(0): p. 75-82.
146. Li, D., et al., *Molybdenum Sulfide/N-Doped CNT Forest Hybrid Catalysts for High Performance Hydrogen Evolution Reaction*. Nano Letters, 2014.
147. Bian, X., et al., *Nanocomposite of MoS₂ on ordered mesoporous carbon nanospheres: A highly active catalyst for electrochemical hydrogen evolution*. Electrochemistry Communications, 2012. **22**(0): p. 128-132.
148. Chen, Z., et al., *Core-shell MoO₃-MoS₂ Nanowires for Hydrogen Evolution: A Functional Design for Electrocatalytic Materials*. Nano Letters, 2011. **11**(10): p. 4168-4175.
149. Kibsgaard, J., et al., *Engineering the surface structure of MoS₂ to preferentially expose active edge sites for electrocatalysis*. Nature Materials, 2012. **11**(11): p. 963-969.
150. Yan, Y., et al., *Ultrathin MoS₂ Nanoplates with Rich Active Sites as Highly Efficient Catalyst for Hydrogen Evolution*. ACS Applied Materials & Interfaces, 2013. **5**(24): p. 12794-12798.
151. Xie, J., et al., *Defect-Rich MoS₂ Ultrathin Nanosheets with Additional Active Edge Sites for Enhanced Electrocatalytic Hydrogen Evolution*. Advanced Materials, 2013. **25**(40): p. 5807-5813.
152. Xie, J., et al., *Controllable Disorder Engineering in Oxygen-Incorporated MoS₂ Ultrathin Nanosheets for Efficient Hydrogen Evolution*. Journal of the American Chemical Society, 2013. **135**(47): p. 17881-17888.
153. Chung, D.Y., et al., *Edge-exposed MoS₂ nano-assembled structures as an efficient electrocatalyst for hydrogen evolution reaction*. Nanoscale, 2013.
154. Wu, Z., et al., *WS₂ nanosheets as a highly efficient electrocatalyst for hydrogen evolution reaction*. Applied Catalysis B: Environmental, 2012. **125**(0): p. 59-66.
155. Cao, L., et al., *Layer-dependent Electrocatalysis of MoS₂ for Hydrogen Evolution*. Nano Letters, 2014.
156. Wang, H., et al., *Electrochemical tuning of vertically aligned MoS₂ nanofilms and its application in improving hydrogen evolution reaction*. Proceedings of the National Academy of Sciences, 2013. **110**(49): p. 19701-19706.
157. Wang, H., et al., *Electrochemical Tuning of MoS₂ Nanoparticles on Three-Dimensional Substrate for Efficient Hydrogen Evolution*. ACS Nano, 2014.
158. Kong, D., et al., *Synthesis of MoS₂ and MoSe₂ Films with Vertically Aligned Layers*. Nano Letters, 2013. **13**(3): p. 1341-1347.
159. Wang, H., et al., *MoSe₂ and WSe₂ Nanofilms with Vertically Aligned Molecular Layers on Curved and Rough Surfaces*. Nano Letters, 2013. **13**(7): p. 3426-3433.
160. Bonde, J., et al., *Hydrogen evolution on nano-particulate transition metal sulfides*. Faraday Discussions, 2009. **140**(0): p. 219-231.

161. Merki, D., et al., *Fe, Co, and Ni ions promote the catalytic activity of amorphous molybdenum sulfide films for hydrogen evolution*. Chemical Science, 2012. **3**(8): p. 2515-2525.
162. Brorson, M., A. Carlsson, and H. Topsøe, *The morphology of MoS₂, WS₂, Co–Mo–S, Ni–Mo–S and Ni–W–S nanoclusters in hydrodesulfurization catalysts revealed by HAADF-STEM*. Catalysis Today, 2007. **123**(1–4): p. 31-36.
163. Lv, X., et al., *Highly Efficient Electrocatalytic Hydrogen Production by Nickel promoted Molybdenum Sulfide microspheres Catalysts*. RSC Advances, 2013.
164. Merki, D., et al., *Amorphous molybdenum sulfide films as catalysts for electrochemical hydrogen production in water*. Chemical Science, 2011. **2**(7): p. 1262-1267.
165. Vrubel, H. and X. Hu, *Growth and Activation of an Amorphous Molybdenum Sulfide Hydrogen Evolving Catalyst*. ACS Catalysis, 2013. **3**(9): p. 2002-2011.
166. Wang, T., et al., *Electrochemically Fabricated Polypyrrole and MoS_x Copolymer Films as a Highly Active Hydrogen Evolution Electrocatalyst*. Advanced Materials, 2014: p. n/a-n/a.
167. Vrubel, H., D. Merki, and X. Hu, *Hydrogen evolution catalyzed by MoS₃ and MoS₂ particles*. Energy & Environmental Science, 2012. **5**(3): p. 6136-6144.
168. Benck, J.D., et al., *Amorphous Molybdenum Sulfide Catalysts for Electrochemical Hydrogen Production: Insights into the Origin of their Catalytic Activity*. ACS Catalysis, 2012. **2**(9): p. 1916-1923.
169. Vrubel, H., et al., *Revealing and accelerating slow electron transport in amorphous molybdenum sulphide particles for hydrogen evolution reaction*. Chemical Communications, 2013. **49**(79): p. 8985-8987.
170. Hsu, C.-L., et al., *Enhancing the electrocatalytic water splitting efficiency for amorphous MoS_x*. International Journal of Hydrogen Energy, 2014. **39**(10): p. 4788-4793.
171. Laursen, A.B., P.C.K. Vesborg, and I. Chorkendorff, *A high-porosity carbon molybdenum sulphide composite with enhanced electrochemical hydrogen evolution and stability*. Chemical Communications, 2013. **49**(43): p. 4965-4967.
172. Morales-Guio, C.G. and X. Hu, *Amorphous Molybdenum Sulfides as Hydrogen Evolution Catalysts*. Accounts of Chemical Research, 2014.
173. Laursen, A.B., et al., *Molybdenum sulfides-efficient and viable materials for electro - and photoelectrocatalytic hydrogen evolution*. Energy & Environmental Science, 2012. **5**(2): p. 5577-5591.
174. Merki, D. and X. Hu, *Recent developments of molybdenum and tungsten sulfides as hydrogen evolution catalysts*. Energy & Environmental Science, 2011. **4**(10): p. 3878-3888.
175. Wang, M., L. Chen, and L. Sun, *Recent progress in electrochemical hydrogen production with earth-abundant metal complexes as catalysts*. Energy & Environmental Science, 2012. **5**(5): p. 6763-6778.
176. Yan, Y., et al., *Recent Development of Molybdenum Sulfides as Advanced Electrocatalysts for Hydrogen Evolution Reaction*. ACS Catalysis, 2014. **4**(6): p. 1693-1705.
177. Morales-Guio, C.G., L.-A. Stern, and X. Hu, *Nanostructured hydrotreating catalysts for electrochemical hydrogen evolution*, DOI: 10.1039/C3CS60468C. Chemical Society Reviews, 2014.
178. Chhina, H., S. Campbell, and O. Kesler, *Thermal and electrochemical stability of tungsten carbide catalyst supports*. Journal of Power Sources, 2007. **164**(2): p. 431-440.

179. Tsirlina, G.A. and O.A. Petrii, *Hydrogen evolution on smooth stoichiometric tungsten and chromium carbides*. *Electrochimica Acta*, 1987. **32**(4): p. 649-657.
180. Ferri, T., D. Gozzi, and A. Latini, *Hydrogen evolution reaction (HER) at thin film and bulk TiC electrodes*. *International Journal of Hydrogen Energy*, 2007. **32**(18): p. 4692-4701.
181. Wirth, S., et al., *Comparative study of IVB–VIB transition metal compound electrocatalysts for the hydrogen evolution reaction*. *Applied Catalysis B: Environmental*, 2012. **126**(0): p. 225-230.
182. Stott, S.J., et al., *Electrochemical properties of core-shell TiC-TiO₂ nanoparticle films immobilized at ITO electrode surfaces*. *Physical Chemistry Chemical Physics*, 2006. **8**(46): p. 5437-5443.
183. Ignaszak, A., et al., *Titanium carbide and its core-shelled derivative TiC@TiO₂ as catalyst supports for proton exchange membrane fuel cells*. *Electrochimica Acta*, 2012. **69**(0): p. 397-405.
184. Hunt, S.T., T. Nimmanwudipong, and Y. Román-Leshkov, *Engineering Non-sintered, Metal-Terminated Tungsten Carbide Nanoparticles for Catalysis*. *Angewandte Chemie International Edition*, 2014: p. n/a-n/a.
185. Yang, X., et al., *Activation of Tungsten Carbide Catalysts by Use of an Oxygen Plasma Pretreatment*. *ACS Catalysis*, 2012. **2**(5): p. 765-769.
186. Kelly, T.G., et al., *Monolayer palladium supported on molybdenum and tungsten carbide substrates as low-cost hydrogen evolution reaction (HER) electrocatalysts*. *International Journal of Hydrogen Energy*, 2013. **38**(14): p. 5638-5644.
187. Kimmel, Y.C., et al., *Effect of surface carbon on the hydrogen evolution reactivity of tungsten carbide (WC) and Pt-modified WC electrocatalysts*. *International Journal of Hydrogen Energy*, 2012. **37**(4): p. 3019-3024.
188. Esposito, D.V., et al., *Low-Cost Hydrogen-Evolution Catalysts Based on Monolayer Platinum on Tungsten Monocarbide Substrates*. *Angewandte Chemie International Edition*, 2010. **49**(51): p. 9859-9862.
189. Esposito, D.V., et al., *A New Class of Electrocatalysts for Hydrogen Production from Water Electrolysis: Metal Monolayers Supported on Low-Cost Transition Metal Carbides*. *Journal of the American Chemical Society*, 2012. **134**(6): p. 3025-3033.
190. Vrubel, H. and X. Hu, *Molybdenum Boride and Carbide Catalyze Hydrogen Evolution in both Acidic and Basic Solutions*. *Angewandte Chemie International Edition*, 2012. **51**(51): p. 12703-12706.
191. Chen, W.-f., et al., *Highly active and durable nanostructured molybdenum carbide electrocatalysts for hydrogen production*. *Energy & Environmental Science*, 2013. **6**(3): p. 943-951.
192. Youn, D.H., et al., *Highly Active and Stable Hydrogen Evolution Electrocatalysts Based on Molybdenum Compounds on Carbon Nanotube–Graphene Hybrid Support*. *ACS Nano*, 2014.
193. Chen, W.-F., et al., *Biomass-derived electrocatalytic composites for hydrogen evolution*. *Energy & Environmental Science*, 2013. **6**(6): p. 1818-1826.
194. Pan, L.F., et al., *Molybdenum Carbide Stabilized on Graphene with High Electrocatalytic Activity for Hydrogen Evolution Reaction*. *Chemical Communications*, 2014.
195. Cui, W., et al., *Mo₂C Nanoparticles Decorated Graphitic Carbon Sheets: Biopolymer-Derived Solid-State Synthesis and Application as an Efficient Electrocatalyst for Hydrogen Generation*. *ACS Catalysis*, 2014: p. 2658-2661.
196. Chen, W.-F., et al., *Tungsten Carbide–Nitride on Graphene Nanoplatelets as a Durable Hydrogen Evolution Electrocatalyst*. *ChemSusChem*, 2014: p. n/a-n/a.

197. Liao, L., et al., *A nanoporous molybdenum carbide nanowire as an electrocatalyst for hydrogen evolution reaction*. Energy & Environmental Science, 2014. **7**(1): p. 387-392.
198. Liu, P. and J.A. Rodriguez, *Catalysts for Hydrogen Evolution from the [NiFe] Hydrogenase to the Ni₂P(001) Surface: The Importance of Ensemble Effect*. Journal of the American Chemical Society, 2005. **127**(42): p. 14871-14878.
199. Guan, Q., et al., *Alternative synthesis of bulk and supported nickel phosphide from the thermal decomposition of hypophosphites*. Journal of Catalysis, 2009. **263**(1): p. 1-3.
200. Bai, J., et al., *Hydrodesulfurization of dibenzothiophene and its hydrogenated intermediates over bulk MoP*. Journal of Catalysis, 2012. **287**(0): p. 161-169.
201. Clark, P., X. Wang, and S.T. Oyama, *Characterization of Silica-Supported Molybdenum and Tungsten Phosphide Hydroprocessing Catalysts by ³¹P Nuclear Magnetic Resonance Spectroscopy*. Journal of Catalysis, 2002. **207**(2): p. 256-265.
202. Liu, P., et al., *Desulfurization Reactions on Ni₂P(001) and α -Mo₂C(001) Surfaces: Complex Role of P and C Sites*. The Journal of Physical Chemistry B, 2005. **109**(10): p. 4575-4583.
203. Tian, J., et al., *Self-Supported Cu₃P Nanowire Arrays as an Integrated High-Performance Three-Dimensional Cathode for Generating Hydrogen from Water*. Angewandte Chemie International Edition, 2014: p. n/a-n/a.
204. Xu, Y., et al., *Anion-exchange synthesis of nanoporous FeP nanosheets as electrocatalysts for hydrogen evolution reaction*. Chemical Communications, 2013. **49**(59): p. 6656-6658.
205. Popczun, E.J., et al., *Nanostructured Nickel Phosphide as an Electrocatalyst for the Hydrogen Evolution Reaction*. Journal of the American Chemical Society, 2013. **135**(25): p. 9267-9270.
206. Popczun, E.J., et al., *Highly Active Electrocatalysis of the Hydrogen Evolution Reaction by Cobalt Phosphide Nanoparticles*. Angewandte Chemie International Edition, 2014: p. n/a-n/a.
207. Xiao, P., et al., *Molybdenum phosphide as an efficient electrocatalyst for hydrogen evolution reaction*. Energy & Environmental Science, 2014. **7**(8): p. 2624-2629.
208. McEnaney, J.M., et al., *Amorphous Molybdenum Phosphide Nanoparticles for Electrocatalytic Hydrogen Evolution*. Chemistry of Materials, 2014.
209. McEnaney, J., et al., *Electrocatalytic Hydrogen Evolution Using Amorphous Tungsten Phosphide Nanoparticles*. Chemical Communications, 2014.
210. Xing, Z., et al., *Closely Interconnected Network of Molybdenum Phosphide Nanoparticles: A Highly Efficient Electrocatalyst for Generating Hydrogen from Water*. Advanced Materials, 2014: p. n/a-n/a.
211. chen, x., et al., *Molybdenum phosphide?A new highly efficient catalyst for the electrochemical hydrogen evolution reaction*. Chemical Communications, 2014.
212. Feng, L., et al., *Easily-prepared dinickel phosphide (Ni₂P) nanoparticles as an efficient and robust electrocatalyst for hydrogen evolution*. Physical Chemistry Chemical Physics, 2014. **16**(13): p. 5917-5921.
213. Tian, J., et al., *Self-Supported Nanoporous Cobalt Phosphide Nanowire Arrays: An Efficient 3D Hydrogen-Evolving Cathode over the Wide Range of pH 0–14*. Journal of the American Chemical Society, 2014. **136**(21): p. 7587-7590.
214. Liu, Q., et al., *Carbon Nanotubes Decorated with CoP Nanocrystals: A Highly Active Non-Noble-Metal Nanohybrid Electrocatalyst for Hydrogen Evolution*. Angewandte Chemie International Edition, 2014: p. n/a-n/a.
215. Gu, S., et al., *Three-dimensional interconnected network of nanoporous CoP nanowires as an efficient hydrogen evolution cathode*. Physical Chemistry Chemical Physics, 2014.

216. Jiang, P., et al., *CoP nanostructures with different morphologies: synthesis, characterization and study of their electrocatalytic performace toward hydrogen evolution reaction*. Journal of Materials Chemistry A, 2014.
217. Pu, Z., et al., *CoP Nanosheet Arrays Supported on Ti Plate: An Efficient Cathode for Electrochemical Hydrogen Evolution*. Chemistry of Materials, 2014.
218. Pu, Z., et al., *Ni₂P nanoparticle films supported on a Ti plate as an efficient hydrogen evolution cathode*. Nanoscale, 2014.
219. Liu, R., et al., *Controlled Synthesis of FeP Nanorod Arrays as Highly Efficient Hydrogen Evolution Cathode*. Journal of Materials Chemistry A, 2014.
220. Oyama, S.T., et al., *Transition metal phosphide hydroprocessing catalysts: A review*. Catalysis Today, 2009. **143**(1–2): p. 94-107.
221. Ichimin, S., et al., *Electrical Conductivity of Nickel Phosphides*. Japanese Journal of Applied Physics, 1993. **32**(S3): p. 294.
222. Cui, W., et al., *Activated carbon nanotubes: a highly-active metal-free electrocatalyst for hydrogen evolution reaction*. Chemical Communications, 2014.
223. Misra, A., J. Giri, and C. Daraio, *Hydrogen Evolution on Hydrophobic Aligned Carbon Nanotube Arrays*. ACS Nano, 2009. **3**(12): p. 3903-3908.
224. Zheng, Y., et al., *Hydrogen evolution by a metal-free electrocatalyst*. Nature communications, 2014. **5**.
225. Zheng, Y., et al., *Toward Design of Synergistically Active Carbon-Based Catalysts for Electrocatalytic Hydrogen Evolution*. ACS Nano, 2014.
226. Zou, X., et al., *Cobalt-Embedded Nitrogen-Rich Carbon Nanotubes Efficiently Catalyze Hydrogen Evolution Reaction at All pH Values*. Angewandte Chemie International Edition, 2014. **53**(17): p. 4372-4376.
227. Maruyama, J., et al., *Hydrogen Evolution by Carbonaceous Nanoparticle Aggregates that were derived from Cobalt Phthalocyanine*. ChemCatChem, 2013. **5**(1): p. 130-133.
228. Maruyama, J., et al., *Carbonaceous Hydrogen-Evolution Catalyst Containing Cobalt Surrounded by a Tuned Local Structure*. ChemCatChem, 2014: p. n/a-n/a.
229. Deng, J., et al., *Highly active and durable non-precious-metal catalyst encapsulated in carbon nanotubes for hydrogen evolution reaction*. Energy & Environmental Science, 2014.
230. Das, R.K., et al., *Extraordinary Hydrogen Evolution and Oxidation Reaction Activity from Carbon Nanotubes and Graphitic Carbons*. ACS Nano, 2014.
231. Hu, B., et al., *From MoO₃ Nanobelts to MoO₂ Nanorods: Structure Transformation and Electrical Transport*. ACS Nano, 2009. **3**(2): p. 478-482.
232. Lanzini, A. and P. Leone, *Experimental investigation of direct internal reforming of biogas in solid oxide fuel cells*. International Journal of Hydrogen Energy, 2010. **35**(6): p. 2463-2476.
233. Tao, S.W., J.T.S. Irvine, and J.A. Kilner, *An Efficient Solid Oxide Fuel Cell Based upon Single-Phase Perovskites*. Advanced Materials, 2005. **17**(14): p. 1734-1737.
234. Atkinson, A., et al., *Advanced anodes for high-temperature fuel cells*. Nature Materials, 2004. **3**(1): p. 17-27.
235. Cowin, P.I., et al., *Recent Progress in the Development of Anode Materials for Solid Oxide Fuel Cells*. Advanced Energy Materials, 2011. **1**(3): p. 314-332.
236. Jiang, S.P., et al., *GDC-impregnated, (La_{0.75}Sr_{0.25})(Cr_{0.5}Mn_{0.5})O₃ anodes for direct utilization of methane in solid oxide fuel cells*. Journal of the Electrochemical Society, 2006. **153**(5): p. A850-A856.
237. Wang, W., et al., *GDC-impregnated Ni anodes for direct utilization of methane in solid oxide fuel cells*. Journal of Power Sources, 2006. **159**(1): p. 68-72.
238. Ge, X.M. and S.H. Chan, *Lanthanum Strontium Vanadate as Potential Anodes for Solid Oxide Fuel Cells*. Journal of the Electrochemical Society, 2009. **156**(3): p. B386-B391.

239. Baldychev, I., et al., *A study of the redox properties and methanol oxidation rates for molybdenum-based mixed oxides*. Applied Catalysis A: General, 2011. **394**(1-2): p. 287-293.
240. Jiang, S.P., et al., *(La_{0.75}Sr_{0.25})(Cr_{0.5}Mn_{0.5})O₃/YSZ composite anodes for methane oxidation reaction in solid oxide fuel cells*. Solid State Ionics, 2006. **177**(1-2): p. 149-157.
241. Mogensen, M., N.M. Sammes, and G.A. Tompsett, *Physical, chemical and electrochemical properties of pure and doped ceria*. Solid State Ionics, 2000. **129**(1-4): p. 63-94.
242. Zhang, Y., et al., *Nanostructured GDC-impregnated La_{0.7}Ca_{0.3}CrO_{3-δ} symmetrical electrodes for solid oxide fuel cells operating on hydrogen and city gas*. International Journal of Hydrogen Energy, 2011. **36**(5): p. 3673-3680.
243. Mohammed Hussain, A., et al., *Nickel-ceria infiltrated Nb-doped SrTiO₃ for low temperature SOFC anodes and analysis on gas diffusion impedance*. International Journal of Hydrogen Energy, 2012. **37**(5): p. 4309-4318.
244. Tao, S. and J.T.S. Irvine, *Investigation of the Mixed Conducting Oxide Sc₂Y₂Zr₂O₁₂ as a Potential SOFC Anode Material*. Journal of the Electrochemical Society, 2004. **151**(4): p. A497-A503.
245. Adler, S.B., *Limitations of charge-transfer models for mixed-conducting oxygen electrodes*. Solid State Ionics, 2000. **135**(1-4): p. 603-612.
246. Barfod, R., et al., *Detailed Characterization of Anode-Supported SOFCs by Impedance Spectroscopy*. Journal of the Electrochemical Society, 2007. **154**(4): p. B371-B378.
247. Vasala, S., H. Yamauchi, and M. Karppinen, *Role of SrMoO₄ in Sr₂MgMoO₆ synthesis*. Journal of Solid State Chemistry, 2011. **184**(5): p. 1312-1317.
248. Petit, C.T.G., et al., *Novel redox reversible oxide, Sr-doped cerium orthovanadate to metavanadate*. Journal of Materials Chemistry, 2011. **21**(2): p. 525-531.
249. Petit, C.T.G., et al., *Structure, conductivity and redox reversibility of Ca-doped cerium metavanadate*. Journal of Materials Chemistry, 2011. **21**(24): p. 8854-8861.
250. Sasaki, K. and J. Maier, *Re-analysis of defect equilibria and transport parameters in Y₂O₃-stabilized ZrO₂ using EPR and optical relaxation*. Solid State Ionics, 2000. **134**(3-4): p. 303-321.
251. Gross, M.D., et al., *Redox Stability of SrNb_xTi_{1-x}O₃-YSZ for Use in SOFC Anodes*. Journal of the Electrochemical Society, 2009. **156**(4): p. B540-B545.
252. Jiang, S.P. and S.P.S. Badwal, *Hydrogen Oxidation at the Nickel and Platinum Electrodes on Ytria-Tetragonal Zirconia Electrolyte*. Journal of the Electrochemical Society, 1997. **144**(11): p. 3777-3784.
253. Ihara, M., T. Kusano, and C. Yokoyama, *Competitive Adsorption Reaction Mechanism of Ni/Ytria-Stabilized Zirconia Cermet Anodes in H₂/H₂O Solid Oxide Fuel Cells*. Journal of The Electrochemical Society, 2001. **148**(3): p. A209-A219.
254. Zheng, L.L., et al., *Effect of Pd-impregnation on performance, sulfur poisoning and tolerance of Ni/GDC anode of solid oxide fuel cells*. International Journal of Hydrogen Energy, 2012. **37**(13): p. 10299-10310.
255. Matsuzaki, Y. and I. Yasuda, *The poisoning effect of sulfur-containing impurity gas on a SOFC anode: Part I. Dependence on temperature, time, and impurity concentration*. Solid State Ionics, 2000. **132**(3-4): p. 261-269.
256. Goodenough, J.B. and Y.-H. Huang, *Alternative anode materials for solid oxide fuel cells*. Journal of Power Sources, 2007. **173**(1): p. 1-10.
257. Park, S., J.M. Vohs, and R.J. Gorte, *Direct oxidation of hydrocarbons in a solid-oxide fuel cell*. Nature, 2000. **404**(6775): p. 265-267.
258. Xiao, G. and F. Chen, *Ni modified ceramic anodes for direct-methane solid oxide fuel cells*. Electrochemistry Communications, 2011. **13**(1): p. 57-59.

259. Kim, G., et al., *SOFC Anodes Based on LST--YSZ Composites and on $Y_{0.04}Ce_{0.48}Zr_{0.48}O_2$* . Journal of the Electrochemical Society, 2008. **155**(4): p. B360-B366.
260. Nishihata, Y., et al., *Self-regeneration of a Pd-perovskite catalyst for automotive emissions control*. Nature, 2002. **418**(6894): p. 164-167.
261. Tanaka, H., et al., *Self-Regenerating Rh- and Pt-Based Perovskite Catalysts for Automotive-Emissions Control*. Angewandte Chemie International Edition, 2006. **45**(36): p. 5998-6002.
262. Goldwasser, M.R., et al., *Perovskites as catalysts precursors: CO₂ reforming of CH₄ on $Ln_{1-x}Ca_xRu_{0.8}Ni_{0.2}O_3$ ($Ln = La, Sm, Nd$)*. Applied Catalysis A: General, 2003. **255**(1): p. 45-57.
263. Navarro, R.M., et al., *Effect of Ru on LaCoO₃ perovskite-derived catalyst properties tested in oxidative reforming of diesel*. Applied Catalysis B: Environmental, 2007. **73**(3-4): p. 247-258.
264. Bu, Y., et al., *Redox stability and sulfur resistance of $Sm_{0.9}Sr_{0.1}Cr_xFe_{1-x}O_{3-\delta}$ perovskite materials*. Journal of Alloys and Compounds, 2013. **578**(0): p. 60-66.
265. Jaiswal, N., et al., *Effect of Mg and Sr co-doping on the electrical properties of ceria-based electrolyte materials for intermediate temperature solid oxide fuel cells*. Journal of Alloys and Compounds, 2013. **577**(0): p. 456-462.
266. Tang, L., et al., *Microwave dielectric properties of tunable $Ba_{0.5}Sr_{0.5}TiO_3$ and scheelite $AMoO_4$ ($A = Ba, Sr$) composite ceramics*. Journal of Alloys and Compounds, 2013. **551**(0): p. 556-561.
267. Cao, X.G. and S.P. Jiang, *Sinterability and conductivity of barium doped aluminium lanthanum oxyapatite $La_{9.5}Ba_{0.5}Si_{5.5}Al_{0.5}O_{26.5}$ electrolyte of solid oxide fuel cells*. Journal of Alloys and Compounds, 2012. **523**(0): p. 127-133.
268. Wang, Y., et al., *Electron Microscopy Study of Novel Ru Doped $La_{0.8}Sr_{0.2}CrO_3$ as Anode Materials for Solid Oxide Fuel Cells (SOFCs)*. Microscopy and Microanalysis, 2007. **13**(SupplementS02): p. 100-101.
269. Madsen, B.D., et al., *Nucleation of nanometer-scale electrocatalyst particles in solid oxide fuel cell anodes*. Journal of Power Sources, 2007. **166**(1): p. 64-67.
270. Yang, C., et al., *Sulfur-Tolerant Redox-Reversible Anode Material for Direct Hydrocarbon Solid Oxide Fuel Cells*. Advanced Materials, 2012. **24**(11): p. 1439-1443.
271. Maekawa, T., et al., *Thermal and electrical properties of perovskite-type strontium molybdate*. Journal of Alloys and Compounds, 2005. **390**(1-2): p. 314-317.
272. Martínez-Coronado, R., et al., *New $SrMo_{1-x}Cr_xO_{3-\delta}$ perovskites as anodes in solid-oxide fuel cells*. International Journal of Hydrogen Energy, 2013(0).
273. Liu, Y., et al., *A stability study of impregnated LSCF-GDC composite cathodes of solid oxide fuel cells*. Journal of Alloys and Compounds, 2013. **578**(0): p. 37-43.
274. Prasad, D.H., et al., *Superior sinterability of nano-crystalline gadolinium doped ceria powders synthesized by co-precipitation method*. Journal of Alloys and Compounds, 2010. **495**(1): p. 238-241.
275. Xiao, P., et al., *H₂ and CH₄ oxidation on $Gd_{0.2}Ce_{0.8}O_{1.9}$ infiltrated $SrMoO_3$ -yttria-stabilized zirconia anode for solid oxide fuel cells*. International Journal of Hydrogen Energy, 2012. **37**(23): p. 18349-18356.
276. Aguadero, A., et al., *A New Family of Mo-Doped $SrCoO_{3-\delta}$ Perovskites for Application in Reversible Solid State Electrochemical Cells*. Chemistry of Materials, 2012. **24**(14): p. 2655-2663.
277. Princivalle, A., et al., *Sintering and conductivity of $BaCe_{0.9}Y_{0.1}O_{2.95}$ synthesized by the sol-gel method*. Journal of Power Sources, 2011. **196**(22): p. 9238-9245.
278. Calderone, V.R., et al., *Size and Shape Control of $SrTiO_3$ Particles Grown by Epitaxial Self-Assembly*. Chemistry of Materials, 2006. **18**(6): p. 1627-1633.

279. Shannon, R., *Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides*. Acta Crystallographica Section A: Foundations of Crystallography, 1976. **32**(5): p. 751-767.
280. Hamada, I., et al., *A Density Functional Theory Study of Self-Regenerating Catalysts $\text{LaFe}_{1-x}\text{M}_x\text{O}_{3-y}$ ($M = \text{Pd}, \text{Rh}, \text{Pt}$)*. Journal of the American Chemical Society, 2011. **133**(46): p. 18506-18509.
281. Huang, Y.-H., et al., *Synthesis and Characterization of $\text{Sr}_2\text{MgMoO}_{6-\delta}$* . Journal of the Electrochemical Society, 2006. **153**(7): p. A1266-A1272.
282. Martínez-Coronado, R., et al., *Optimized energy conversion efficiency in solid-oxide fuel cells implementing $\text{SrMo}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ perovskites as anodes*. Journal of Power Sources, 2012. **208**(0): p. 153-158.
283. Zhang, L., et al., *Double-perovskites $\text{A}_2\text{FeMoO}_{6-\delta}$ ($A = \text{Ca}, \text{Sr}, \text{Ba}$) as anodes for solid oxide fuel cells*. Journal of Power Sources, 2010. **195**(19): p. 6356-6366.
284. Kobsiriphat, W., et al., *Nickel and Ruthenium-Doped Lanthanum Chromite Anodes: Effects of Nanoscale Metal Precipitation on Solid Oxide Fuel Cell Performance*. Journal of the Electrochemical Society, 2010. **157**(2): p. B279-B284.
285. Le Goff, A., et al., *From Hydrogenases to Noble Metal-Free Catalytic Nanomaterials for H_2 Production and Uptake*. Science, 2009. **326**(5958): p. 1384-1387.
286. Dresselhaus, M.S. and I.L. Thomas, *Alternative energy technologies*. Nature, 2001. **414**(6861): p. 332-337.
287. Chen, W.-F., et al., *Hydrogen-Evolution Catalysts Based on Non-Noble Metal Nickel-Molybdenum Nitride Nanosheets*. Angewandte Chemie International Edition, 2012. **51**(25): p. 6131-6135.
288. Yan, Y., et al., *Template-Free Pseudomorphic Synthesis of Tungsten Carbide Nanorods*. Small, 2012. **8**(21): p. 3350-3356.
289. Antolini, E., *Platinum-based ternary catalysts for low temperature fuel cells: Part II. Electrochemical properties*. Applied Catalysis B: Environmental, 2007. **74**(3-4): p. 337-350.
290. Antolini, E., *Platinum-based ternary catalysts for low temperature fuel cells: Part I. Preparation methods and structural characteristics*. Applied Catalysis B: Environmental, 2007. **74**(3-4): p. 324-336.
291. Serov, A. and C. Kwak, *Review of non-platinum anode catalysts for DMFC and PEMFC application*. Applied Catalysis B: Environmental, 2009. **90**(3-4): p. 313-320.
292. Evans, D.J. and C.J. Pickett, *Chemistry and the hydrogenases*. Chemical Society Reviews, 2003. **32**(5): p. 268-275.
293. Volbeda, A. and J.C. Fontecilla-Camps, *The active site and catalytic mechanism of NiFe hydrogenases*. Dalton Transactions, 2003(21): p. 4030-4038.
294. Harnisch, F., G. Sievers, and U. Schröder, *Tungsten carbide as electrocatalyst for the hydrogen evolution reaction in pH neutral electrolyte solutions*. Applied Catalysis B: Environmental, 2009. **89**(3-4): p. 455-458.
295. Harnisch, F., et al., *Electrocatalytic and corrosion behaviour of tungsten carbide in near-neutral pH electrolytes*. Applied Catalysis B: Environmental, 2009. **87**(1-2): p. 63-69.
296. McKone, J.R., et al., *Ni-Mo Nanopowders for Efficient Electrochemical Hydrogen Evolution*. ACS Catalysis, 2012: p. 166-169.
297. Coleman, J.N., et al., *Two-Dimensional Nanosheets Produced by Liquid Exfoliation of Layered Materials*. Science, 2011. **331**(6017): p. 568-571.
298. Eda, G., et al., *Photoluminescence from Chemically Exfoliated MoS_2* . Nano Letters, 2011. **11**(12): p. 5111-5116.
299. Shi, C., et al., *Ni-modified Mo_2C catalysts for methane dry reforming*. Applied Catalysis A: General, 2012. **431-432**(0): p. 164-170.

300. Lausche, A.C., J.A. Schaidle, and L.T. Thompson, *Understanding the effects of sulfur on Mo₂C and Pt/Mo₂C catalysts: Methanol steam reforming*. Applied Catalysis A: General, 2011. **401**(1–2): p. 29-36.
301. Han, J., et al., *Carbon-Supported Molybdenum Carbide Catalysts for the Conversion of Vegetable Oils*. ChemSusChem, 2012. **5**(4): p. 727-733.
302. Schaidle, J.A., A.C. Lausche, and L.T. Thompson, *Effects of sulfur on Mo₂C and Pt/Mo₂C catalysts: Water gas shift reaction*. Journal of Catalysis, 2010. **272**(2): p. 235-245.
303. Gao, Q., et al., *Synthesis of Nanoporous Molybdenum Carbide Nanowires Based on Organic–Inorganic Hybrid Nanocomposites with Sub-Nanometer Periodic Structures*. Chemistry of Materials, 2009. **21**(23): p. 5560-5562.
304. Gao, Q., et al., *One-dimensional growth of MoOx-based organic-inorganic hybrid nanowires with tunable photochromic properties*. Journal of Materials Chemistry, 2012. **22**(11): p. 4709-4715.
305. Toksoz, S., H. Acar, and M.O. Guler, *Self-assembled one-dimensional soft nanostructures*. Soft Matter, 2010. **6**(23): p. 5839-5849.
306. Lasocha, W., J. Jansen, and H. Schenk, *Crystal Structure of Fibrillar Anilinum Trimolybdate 2(C₆H₅NH₃) · Mo₃O₁₀ · 4H₂O from X-Ray Powder Data*. Journal of Solid State Chemistry, 1995. **117**(1): p. 103-107.
307. Oshikawa, K., M. Nagai, and S. Omi, *Characterization of Molybdenum Carbides for Methane Reforming by TPR, XRD, and XPS*. Journal of Physical Chemistry B, 2001. **105**(38): p. 9124-9131.
308. Brox, B. and I. Olefjord, *ESCA Studies of MoO₂ and MoO₃*. Surface and Interface Analysis, 1988. **13**(1): p. 3-6.
309. Singh, V., et al., *Graphene based materials: Past, present and future*. Progress in Materials Science, 2011. **56**(8): p. 1178-1271.
310. Dresselhaus, M.S., et al., *Perspectives on Carbon Nanotubes and Graphene Raman Spectroscopy*. Nano Letters, 2010. **10**(3): p. 751-758.
311. Frauwallner, M.-L., et al., *Toluene hydrogenation at low temperature using a molybdenum carbide catalyst*. Applied Catalysis A: General, 2011. **394**(1–2): p. 62-70.
312. Becerril, H.A., et al., *Evaluation of Solution-Processed Reduced Graphene Oxide Films as Transparent Conductors*. ACS Nano, 2008. **2**(3): p. 463-470.
313. Jiang, S.P., et al., *Electrical conductivity and performance of doped LaCrO₃ perovskite oxides for solid oxide fuel cells*. Journal of Power Sources, 2008. **176**(1): p. 82-89.
314. Zhou, W., et al., *Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} + LaCoO₃ composite cathode for Sm_{0.2}Ce_{0.8}O_{1.9}-electrolyte based intermediate-temperature solid-oxide fuel cells*. Journal of Power Sources, 2007. **168**(2): p. 330-337.
315. Nørskov, J.K., et al., *Trends in the Exchange Current for Hydrogen Evolution*. Journal of the Electrochemical Society, 2005. **152**(3): p. J23-J26.
316. Huot, J.Y., M.L. Trudeau, and R. Schulz, *Low Hydrogen Overpotential Nanocrystalline Ni - Mo Cathodes for Alkaline Water Electrolysis*. Journal of the Electrochemical Society, 1991. **138**(5): p. 1316-1321.
317. Huot, J.Y. and L. Brossard, *Time dependence of the hydrogen discharge at 70°C on nickel cathodes*. International Journal of Hydrogen Energy, 1987. **12**(12): p. 821-830.
318. Chen, W.-F., J.T. Muckerman, and E. Fujita, *Recent developments in transition metal carbides and nitrides as hydrogen evolution electrocatalysts*. Chemical Communications, 2013. **49**(79): p. 8896-8909.
319. Kong, D., et al., *CoSe₂ Nanoparticles Grown on Carbon Fiber Paper: An Efficient and Stable Electrocatalyst for Hydrogen Evolution Reaction*. Journal of the American Chemical Society, 2014. **136**(13): p. 4897-4900.

320. Kong, D., et al., *First-row transition metal dichalcogenide catalysts for hydrogen evolution reaction*. Energy & Environmental Science, 2013. **6**(12): p. 3553-3558.
321. Hunt, S.T., T. Nimmanwudipong, and Y. Román-Leshkov, *Engineering Non-sintered, Metal-Terminated Tungsten Carbide Nanoparticles for Catalysis*, DOI: 10.1002/anie.201400294. Angewandte Chemie International Edition, 2014.
322. Wan, C., Y.N. Regmi, and B.M. Leonard, *Multiple Phases of Molybdenum Carbide as Electrocatalysts for the Hydrogen Evolution Reaction*, DOI: 10.1002/anie.201402998. Angewandte Chemie International Edition, 2014.
323. Liu, Q., et al., *Carbon Nanotubes Decorated with CoP Nanocrystals: A Highly Active Non-Noble-Metal Nanohybrid Electrocatalyst for Hydrogen Evolution*, DOI: 10.1002/anie.201404161. Angewandte Chemie International Edition, 2014.
324. Popczun, E.J., et al., *Highly Active Electrocatalysis of the Hydrogen Evolution Reaction by Cobalt Phosphide Nanoparticles*. Angewandte Chemie International Edition, 2014. **53**(21): p. 5427-5430.
325. Xiao, P., et al., *Investigation of molybdenum carbide nano-rod as an efficient and durable electrocatalyst for hydrogen evolution in acidic and alkaline media*. Applied Catalysis B: Environmental, 2014. **154–155**(0): p. 232-237.
326. Gu, Z., et al., *Large-scale synthesis of single-crystal hexagonal tungsten trioxide nanowires and electrochemical lithium intercalation into the nanocrystals*. Journal of Solid State Chemistry, 2007. **180**(1): p. 98-105.
327. Hwu, H.H. and J.G. Chen, *Surface Chemistry of Transition Metal Carbides*. Chemical Reviews, 2004. **105**(1): p. 185-212.
328. Zhao, X., et al., *Interconnected core-shell MoO₂ microcapsules with nanorod-assembled shells as high-performance lithium-ion battery anodes*. Journal of Materials Chemistry, 2012. **22**(26): p. 13334-13340.
329. Marin Flores, O.G. and S. Ha, *Activity and stability studies of MoO₂ catalyst for the partial oxidation of gasoline*. Applied Catalysis A: General, 2009. **352**(1–2): p. 124-132.
330. Thomas, J.G.N., *Kinetics of electrolytic hydrogen evolution and the adsorption of hydrogen by metals*. Transactions of the Faraday Society, 1961. **57**(0): p. 1603-1611.
331. Shen, J., et al., *How carboxylic groups improve the performance of single-walled carbon nanotube electrochemical capacitors?* Energy & Environmental Science, 2011. **4**(10): p. 4220-4229.
332. Chen, Y., et al., *Fe₃O₄ Nanoparticles Embedded in Uniform Mesoporous Carbon Spheres for Superior High-Rate Battery Applications*. Advanced Functional Materials, 2014. **24**(3): p. 319-326.
333. Cammack, R., *Bioinorganic chemistry: Hydrogenase sophistication*. Nature, 1999. **397**(6716): p. 214-215.
334. Shima, S., et al., *The Crystal Structure of [Fe]-Hydrogenase Reveals the Geometry of the Active Site*. Science, 2008. **321**(5888): p. 572-575.
335. Karunadasa, H.I., C.J. Chang, and J.R. Long, *A molecular molybdenum-oxo catalyst for generating hydrogen from water*. Nature, 2010. **464**(7293): p. 1329-1333.
336. Tran, P.D., et al., *Noncovalent Modification of Carbon Nanotubes with Pyrene-Functionalized Nickel Complexes: Carbon Monoxide Tolerant Catalysts for Hydrogen Evolution and Uptake*. Angewandte Chemie International Edition, 2011. **50**(6): p. 1371-1374.
337. Hatay, I., et al., *Hydrogen evolution at polarised liquid/liquid interfaces catalyzed by molybdenum disulfide*. Energy & Environmental Science, 2011. **4**(10): p. 4246-4251.
338. Chianelli, R.R., et al., *Catalytic Properties of Single Layers of Transition Metal Sulfide Catalytic Materials*. Catalysis Reviews: Science and Engineering, 2006. **48**(1): p. 1-41.

-
339. Schmickler, W. and S. Trasatti, *Comment on "Trends in the Exchange Current for Hydrogen Evolution"* [*J. Electrochem. Soc.*, 152, J23 (2005)]. *Journal of The Electrochemical Society*, 2006. **153**(12): p. L31-L32.
340. Nørskov, J.K., et al., *Response to "Comment on 'Trends in the Exchange Current for Hydrogen Evolution' [J. Electrochem. Soc. , 152 , J23 (2005)]"*. *Journal of The Electrochemical Society*, 2006. **153**(12): p. L33.
341. Kresse, G. and J. Furthmüller, *Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set*. *Physical Review B*, 1996. **54**(16): p. 11169-11186.
342. Kresse, G. and J. Hafner, *Ab initio molecular dynamics for open-shell transition metals*. *Physical Review B*, 1993. **48**(17): p. 13115-13118.
343. Kresse, G. and J. Furthmüller, *Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set*. *Computational Materials Science*, 1996. **6**(1): p. 15-50.
344. Perdew, J.P., K. Burke, and M. Ernzerhof, *Generalized Gradient Approximation Made Simple*. *Physical Review Letters*, 1996. **77**(18): p. 3865-3868.
345. Blöchl, P.E., *Projector augmented-wave method*. *Physical Review B*, 1994. **50**(24): p. 17953-17979.
346. Kresse, G. and D. Joubert, *From ultrasoft pseudopotentials to the projector augmented-wave method*. *Physical Review B*, 1999. **59**(3): p. 1758-1775.
347. Atkins, P.W., *Physical Chemistry*. 1998, Oxford: Oxford University Press.
348. Phillips, D.C., et al., *Synthesis, Characterization, and Hydrodesulfurization Properties of Silica-Supported Molybdenum Phosphide Catalysts*. *Journal of Catalysis*, 2002. **207**(2): p. 266-273.

List of Publications:

P. Xiao, X. Ge, H. Wang, Z. Liu, A. Fisher, X. Wang, Novel Molybdenum Carbide-Tungsten Carbide Composite Nanowires and Their Electrochemical Activation for Efficient and Stable Hydrogen Evolution, *Advanced Functional Materials*, 2015, **25**, p.1520-1526.

P. Xiao, M. A. Sk, L. Thia, X. Ge, R. J. Lim, J.-Y. Wang, K. H. Lim and X. Wang, Molybdenum phosphide as an efficient electro-catalyst for the hydrogen evolution reaction. *Energy & Environmental Science*, 2014, 7, 2624-2629.

P. Xiao, Y. Yan, X. Ge, Z. Liu, J.-Y. Wang, & X. Wang,. Investigation of molybdenum carbide nano-rod as an efficient and durable electrocatalyst for hydrogen evolution in acidic and alkaline media. *Applied Catalysis B: Environmental*, 2014 154–155(0), 232-237.

P. Xiao, X. Ge, Z. Liu, J.-Y. Wang, X. Wang, $\text{Sr}_{1-x}\text{Ca}_x\text{MoO}_3\text{--Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ as the anode in solid oxide fuel cells: Effects of Mo precipitation. *Journal of Alloys and Compounds*, 2014 587(0), 326-331.

P. Xiao, X. Ge, L. Zhang, J.-M. Lee, J.-Y. Wang, X. Wang, H_2 and CH_4 oxidation on $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ infiltrated $\text{SrMoO}_3\text{--yttria-stabilized zirconia}$ anode for solid oxide fuel cells. *International Journal of Hydrogen Energy* 2012, 37 (23), 18349-18356.

T. Wu, H.M. Zhou, B.Y. Xia, **P. Xiao**, Y. Yan, M.S. Xie, X. Wang, Facile Synthesis of 3 D Platinum Dendrites with a Clean Surface as Highly Stable Electrocatalysts, *ChemCatChem*, **6** (2014) 1538-1542

X. Ge; Y. Liu, F. W. Thomas Goh, T. S Andy Hor, Y. Zong, **P. Xiao**, Z. Zhang, B. Li, X. Wang, Z. Liu, Dual-phase Spinel MnCo_2O_4 for Electro-catalytic Oxygen Reduction and Evolution, *ACS Applied Materials & Interfaces*, 2014, 6 (15), pp 12684–12691.

X. Ge, F.W. Goh, B. Li, T.S. Hor, J. Zhang, **P. Xiao**, X. Wang, Y. Zong, Z. Liu, Efficient and durable oxygen reduction and evolution of a hydrothermally synthesized $\text{La}(\text{Co}_{0.55}\text{Mn}_{0.45})_{0.99}\text{O}_{3-\sigma}$ nanorod/graphene hybrid in alkaline media, *Nanoscale*, **7** (2015) 9046-9054.