Surface design of transition-metal based electrocatalysts for high energy storage devices

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NANYANG
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**SURFACE DESIGN OF TRANSITION-METAL
BASED ELECTROCATALYSTS FOR HIGH
ENERGY STORAGE DEVICES**

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**INTERDISCIPLINARY GRADUATE SCHOOL
ENERGY RESEARCH INSTITUTE @ NTU (ERI@N)**

2016

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BASED ELECTROCATALYSTS FOR HIGH
ENERGY STORAGE DEVICES**

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Interdisciplinary Graduate School
Energy Research Institute @ NTU (ERI@N)

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

2016

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

... 25/7/2016. ...
Date

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Abstract

High energy storage devices (*e.g.* Li-O₂ batteries and hydrogen fuel cell) have much larger theoretical specific energy over the commercial Li-ion batteries. However, majority of the energy losses incurred in these high energy storage devices are induced by the overpotential in electrocatalysis due to the sluggish reaction kinetics. Therefore, there is an urge to enhance the reaction kinetics so as to achieve maximum energy efficiency.

The aim for this research is to embellish the reaction kinetics of electrochemical reaction, curtail the activation polarization of the electrochemical reaction and improve the energy efficiency of these high energy storage devices by rational-design of the transition-metal based electrocatalysts (TMBE) via the scope as listed in the following: (1) improve the wetting property of TMBE by deposition of metal oxide (*e.g.* IrO₂ and CuO) onto noble metal (*e.g.* Pt) for Li-O₂ battery; (2) accelerate the proton diffusion rate by fabricating microporous TMBE (*e.g.* microporous Mo₂C) for hydrogen evolution reaction (HER); (3) introduce synergistic effect by co-doping (*e.g.* nitrogen and sulfur) TMBE (*e.g.* Mo₂C) to manipulate the metal-adsorbate electronic structure for HER.

Previously, the fabrication of IrO₂ nanoparticles (NPs) deposited on Pt nanowires (NWs) was employed as an electrocatalyst to establish the “wetting” behavior between metal oxides and the Li₂O₂ for Li-O₂ battery applications. With the presence of IrO₂, the deposition of Li₂O₂ thin layer on the IrO₂/Pt cathode during the discharging process was being observed for the first time. IrO₂ appeared to exhibit a strong affinity with the Li₂O₂ on the electrode. Without such metal oxide-Li₂O₂ interfacial interaction for bare Pt, large Li₂O₂ NPs were formed when Li-O₂ battery was being discharged. The formation of Li₂O₂ thin layer was vital in Li-O₂ battery as it facilitated fast electron transport for oxygen evolution reaction (OER), therefore lowered the charging potential of Li-O₂ battery. In the later stages of study, we explored the flexibility of this “wetting”

system by replacing expensive IrO_2 with other low-cost metal oxide (*e.g.* CuO). Interestingly, such “wetting” phenomenon of $\text{CuO-Li}_2\text{O}_2$ could also be noticed on the CuO/Pt electrode during discharging.

Pt is a preeminent electrocatalyst for numerous electrochemical reactions, such as OER and HER due to its low overpotential in driving the electrochemical reactions. However, being a scarce natural resource, Pt is expensive which confines its practical implementation. Therefore, finding an economical and efficient non-noble metal electrocatalysts is advantageous to achieve scalable production. Recently, Mo_2C has emerged to be an alternative non-Pt electrocatalyst due to its similar d-band electronic structure with Pt. Based on the literatures, Mo_2C material also exhibited excellent electrical conductivity and chemical stability. Inspired by these advantages of the intrinsic properties of Mo_2C material, we have fabricated microporous Mo_2C versus mesoporous Mo_2C for HER. For the first time, we observed that the microporous Mo_2C exhibited much lower HER overpotential as compared to mesoporous Mo_2C electrocatalyst. We could therefore propose that the microporous Mo_2C facilitated a faster proton transport than the latter and thus improved the HER kinetics.

Lastly, we modified the electronic structure of the Mo_2C electrocatalysts by chemically co-doped with heteroatoms, such as nitrogen (N) and sulfur (S). The N/S co-doped Mo_2C exhibits better HER activity as compared to singly doped Mo_2C (*e.g.* S-doped Mo_2C and N-doped Mo_2C) and pure Mo_2C . We therefore proposed that the dual dopants (N/S) in the Mo_2C co-activated the Mo center, exhibiting a synergistic effect (σ -donation and π -back donation), which improved the catalyst-adsorbate interaction, destabilized the H-O bond of H_3O^+ and promoted the formation of H_2 molecules.

In conclusion, the overpotential of the electrochemical reactions could be lowered by the aforementioned rational-designs of the electrocatalysts. Thus, the energy efficiency of their respective energy storage devices could be improved.

Acknowledgements

“Research is to see what everybody else has seen, and to think what nobody else has though”- Albert Szerit-Gyorgyl

“Doing research has never been an easy task. You need to think outside the box and you will encounter infinity number of failure experiments before creating the one that works. But no matter what is the outcome, life still goes on!”

- Ang Huixiang

I feel honored to have supervised under two brilliant supervisors. I would wish to express my thankfulness to my main supervisor, Professor Alex Yan Qingyu and my co-supervisor Professor Chen Hongyu. To Professor Alex Yan Qingyu: First and foremost, thank you for accepting me as your PhD student, working in your research group. Thank you for introducing me into the field of renewable energy storage. Thank you for your patience in guiding and expertise throughout my PhD study. Thank you for encouraging me and leading me from darkness to light. Thank you for all the support and trust you have given to me, giving me tons of freedom to let my imagination outrun my knowledge. To my co-supervisor Professor Chen Hongyu: Thank you all your advices and knowledges you have given me in my research work. There is a Chinese saying, *“good pupils are to be brought up by strict teachers”*. You make me accept my limits and try to go beyond them, nurturing me to become a better scientist.

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“Passion makes us stronger than we are. Love makes us better than we are. Be passionate about the things you love.”-Galen Watson

Table of Contents

Abstract	i
Acknowledgements	iii
Table of Contents	v
Table Captions	xi
Figure Captions.....	xiii
Calculation Captions	xxix
Abbreviations	xxxi
Major Symbols	xxxv
 Chapter 1 Introduction.....	 1
1.1 Problem statements/Hypotheses/Design and performance targets	2
1.2 Objective and scope	4
1.3 Dissertation overview.....	5
1.4 Major findings and outcomes/originality	6
1.5 References	7
 Chapter 2 Literature Review	 9
2.1 Overview	10
2.1.1 Topic 1 Literature review on the wetting property of the TMBE for electrocatalysis	20

2.1.2	Topic 2 Literature review on the nanostructured porous TMBE for electrocatalysis	24
2.1.3	Topic 3 Literature review on the electronic structure of metal-adsorbate for HER	29
2.2	Question to answer and PhD in context based on Topic 1	35
2.3	Question to answer and PhD in context based on Topic 2	36
2.4	Question to answer and PhD in context based on Topic 3	37
2.5	References	39
Chapter 3	Experimental Methodology	47
3.1	Rationale for the selection of materials and methods	48
3.1.1	Selection of materials	48
3.1.2	Selection of synthesis methods	49
3.1.3	Selection of characterization techniques	50
3.2	Principles of synthesis methods	51
3.2.1	Thermal decomposition/Calcination/Carburization	51
3.2.2	Electrochemical deposition	52
3.2.3	Hydrothermal versus solvothermal reaction	52
3.2.4	Precipitation versus crystallization	53
3.2.5	Solvent exfoliation	53
3.3	Principles and analyses of characterization techniques	54
3.3.1	Scanning Electron Microscopy (SEM)/Transmission Electron Microscopy (TEM)	54
3.3.2	Atomic Force Microscopy (AFM)	56
3.3.3	X-Ray Diffraction (XRD)	57
3.3.4	X-Ray Photoelectron Spectroscopy (XPS)	58
3.3.5	Inductively Coupled Plasma – Optical Emission Spectrometer (ICP – OES)	60
3.3.6	¹ H and ¹³ C Nuclear Magnetic Resonance (NMR)	62
3.3.7	Brunauer-Emmett-Teller (BET)	64

3.3.8	Contact angle measurement	65
3.3.9	Linear sweep potential (LSV), Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS), Battery tester	66
3.4	References	69

Chapter 4 Improved Wetting of Li₂O₂ on the Metal Oxide/Pt Oxygen Cathodes for High Performance Lithium-Oxygen Batteries 73

4.1	Introduction.....	74
4.2	Experimental methods	76
4.2.1	Chemicals and materials	76
4.2.2	Synthesis of Pt NWs, IrO ₂ /Pt NWs, and CuO/Pt NWs.....	76
4.2.3	Synthesis of network CuO/Pt NSs on SSM	77
4.2.4	Materials characterizations.....	77
4.2.5	Electrochemical measurements.....	78
4.3	Principle Outcomes	79
4.3.1	Preliminary results for “wetting” study of MO/Pt cathode for Li-O ₂ battery	79
4.3.2	Synthesis and characterizations of CuO/Pt NSs on SSM for Li-O ₂ battery	83
4.3.3	Comparison of the electrochemical performances of CuO/Pt NSs versus Pt NSs batteries	91
4.4	Conclusions	99
4.5	References	100

Chapter 5 Microporous Mo₂C for Efficient Hydrogen Production 103

5.1	Introduction.....	104
5.2	Experimental methods	105
5.2.1	Chemicals and materials	105
5.2.2	Synthesis of carbon-based materials	106
5.2.3	Synthesis of Mo ₂ C electrocatalysts	106

5.2.4	Materials characterizations.....	106
5.2.5	Electrochemical measurements.....	107
5.3	Principle Outcomes	108
5.3.1	Synthesis and characterizations of porous Mo ₂ C materials	108
5.3.2	Comparison of the HER performances of microporous Mo ₂ C versus mesoporous Mo ₂ C electrocatalysts	114
5.3.3	Proposed HER mechanisms for microporous Mo ₂ C versus mesoporous Mo ₂ C electrocatalysts	122
5.4	Conclusions	123
5.5	References	124

Chapter 6 Tuning the Electronic Structure of N/S dual doped Mo₂C for Efficient Hydrogen Production 127

6.1	Introduction.....	128
6.2	Experimental methods	130
6.2.1	Chemicals and materials	130
6.2.2	Synthesis of the layered MoO _x /C/dopant.....	130
6.2.3	Synthesis of the layered undoped/doped Mo ₂ C	130
6.2.4	Exfoliation of layered Mo ₂ C sheets	130
6.2.5	Materials characterizations.....	131
6.2.6	Electrochemical measurements.....	131
6.3	Principle Outcomes	132
6.3.1	Synthesis and characterizations of N and S doped Mo ₂ C	132
6.3.2	Comparison of the HER performances of N and S doped Mo ₂ C	138
6.3.3	Proposed HER mechanisms for N and S doped Mo ₂ C	142
6.4	Conclusions	144
6.5	References	145

Chapter 7	Discussion and Future Works	149
7.1	General Discussion	150
7.1.1	Outcome reflected on hypothesis #1	151
7.1.2	Outcome reflected on hypothesis #2	152
7.1.3	Outcome reflected on hypothesis #3	152
7.2	Reconnaissance works, future works, and outstanding questions	153
7.2.1	Future work #1: Photocatalytic Li-O ₂ battery	154
7.2.2	Outstanding question for future work #1: How can we lower the charging voltage of Li-O ₂ battery using solar light?	155
7.2.3	Future work #2: Electrochemical tuning of M-doped (M: Fe, Co, Ni) W ₂ C for HER	157
7.2.4	Outstanding question for future work #2: How do we improve the HER activity by doping M (M: Fe, Co, Ni) into W ₂ C lattice?	158
7.3	References	160
Appendix		161
Appendix 1:	Supplementary information for Chapter 4	161
Appendix 2:	Supplementary information for Chapter 5	162
Appendix 3:	Supplementary information for Chapter 6	167
References		172
List of Publications		175
Journal articles		175
Conference presentation		177

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Table Captions

Table 2.1 Summary of the various types of HER pathways in acidic and alkaline media.

Table 3.1 Limitations of XRD analysis.

Table 3.2 Advantages and disadvantages of XPS analysis. Table 3.2 obtained from reference ^[33].

Table A.1 The total specific capacity of Li-O₂ batteries with electrodes (*e.g.* Pt NSs and CuO/Pt NSs) during the 1st full discharge at various current density. ^aMeasured specific capacity taken from Figure 4.17a and b. ^bTotal specific capacity calculated based on Calculation A.1.

Table A.2 Operating HER overpotential of different Mo-related materials reported previously.

Table A.3 Elemental composition of the as-prepared Mo₂C/C_{support} sample derived from ICP-OES elemental analysis and CHNS elemental analyzer.

Table A.4 Comparison of HER performances of the electrocatalysts in 0.5 M H₂SO₄ with their respective SSAs and dominant PSDs peak width

Table A.5 Onset overpotentials and operating potentials at current density (*j*) of the electrocatalysts in this work in comparison with the reported values.

Table A.6 Summary of S dopant, N dopant, N/S dopant, C sources and Mo precursors used during hydrothermal reaction.

Table A.7 Element composition of the as-prepared nanosheets samples derived from CHNS elemental analyzer and ICP analysis.

Table A.8 HER performances of different electrocatalysts.

Table A.9 Summary of ΔG_{H^*} values versus the exchange current densities (i_0) of different electrocatalysts from the literature in comparison with the electrocatalysts in this work.

Figure Captions

Figure 2.1 Ragone plot (x-axis: specific energy versus y-axis: specific power) of various energy storage devices. The Ragone plot is reproduced from reference [Atsushi, Tsutsumi. “Fuel Cell/Battery System.” *UTokyo Research*. The University of Tokyo, 13 August 2013. Published. <http://www.u-tokyo.ac.jp/en/utokyo-research/editors-choice/fuel-cellbattery-system/1> June 2016 Accessed.][^{10]} Copyright Atsushi Tsutsumi.

Figure 2.2 (a) Storage and conversion mechanisms for a non-aqueous Li-O₂ battery. (b) Schematic illustration on the thermodynamic potential of OER/ORR: $2\text{Li}^+ + 2\text{e}^- + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2$ is ~ 0 V *versus* NHE (equivalent to 2.96 V *versus* Li⁺/Li). (c) During discharging, Li⁺ ions from the anode undergo reduction with O₂ molecules from the cathode, forming Li₂O₂ on the cathode and this process is called ORR. (d) During charging, the Li₂O₂ on the cathode surface undergoes OER, forming Li⁺ ions and O₂ molecules.

Figure 2.3 (a) The mechanisms of electrolyzer and fuel cell on storage and conversion. (b) Schematic illustration of the thermodynamic potentials of OER/ORR: $\text{O}_2 + 4\text{e}^- + 4\text{H}^+ \leftrightarrow \text{H}_2\text{O}$ at 1.23 V *versus* NHE and thermodynamic potentials of HER/HOR: $4\text{e}^- + 4\text{H}^+ \leftrightarrow 2\text{H}_2$ at 0 V *versus* NHE. (c) To store energy, an electrolyzer is used to split water molecule into energy carriers (*e.g.* H₂ and O₂). (d) For energy conversion, a fuel cell is used to recombine O₂ and H₂ back to H₂O, while releasing energy for consumption.

Figure 2.4 (a) Voltage versus capacity profiles of Li-O₂ batteries with PtAu/C, Pt/C, Au/C at 100 mA g⁻¹, and C at 80 mA g⁻¹. Reproduced with permission from [³⁴]. Copyright © 2010. American Chemical Society. (b) Voltage profiles of Li-O₂ batteries with Pt NPs@CNT at 250 mA g⁻¹. Reproduced with permission from [⁴⁴]. Copyright © 2014. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

(c) Voltage versus capacity profiles of Li-O₂ battery with Mo₂C/CNT at different current density. Reproduced with permission from ^[45]. Copyright © 2015. American Chemical Society. (d) Polarization curves of Mo-based material versus Pt/C for HER. Reproduced with permission from ^[46]. Copyright © 2013. The Royal Society of Chemistry.

Figure 2.5 Heterogeneous redox reaction occurs at the electrode-electrolyte interface.

Figure 2.6 Schematic illustration of the ΔG_{rxn} and $\Delta G^\ddagger$ during reaction progress.

Figure 2.7 Cell overpotentials versus operating current.

Figure 2.8 (a) In general, metal oxides are hydrophilic as their electronic structure favors the formation of H-bond with H₂O molecules. For example, the oxide at the surface of the Al₂O₃ forms H-bond with the H atom on the H₂O molecule, while the empty (3p) orbital of Al atom at the surface of Al₂O₃ is electron deficient and it interacts with the O atom on the H₂O molecule. These strong interactions lead to a contact angle of <10° being obtained, indicating that the Al₂O₃ is hydrophilic in nature. (b) On the other hand, the empty orbital on (4f) inner shell of R³⁺ on the surface of the R₂O₃ are shielded by the octet outer 5s and 5p orbitals, which hidden the interaction between the O atom on H₂O and R³⁺. As a result, a contact angle of ~102° is obtained, representing that the R₂O₃ is hydrophobic in nature. (a-b) Reproduced with permission from ^[55]. Copyright © 2013. Nature Publishing Group.

Figure 2.9 Contact angles (θ) measured experimentally as a function of the logarithm of the molar fraction of oxygen dissolved ($\log X_o$) associated with MO. Reproduced with permission from ^[72]. Copyright © 2001. Elsevier Science.

Figure 2.10 Schematics illustration of the nucleation and growth pathways of newly formed ZnO adsorbate (represented by green color) on the existing Au-ZnO substrate (ZnO represents as blue color) and Au represents as red color) at a condition when the interfacial energy of adsorbate-substrate is (a) high or (b) low. γ_{33} represents the surface energy of existing ZnO and newly formed ZnO via path A and γ_{13} represents the surface energy of existing Au and newly formed ZnO via path B. (a-b) Reproduced with permission from ^[79]. Copyright © 2013. American Chemical Society.

Figure 2.11 N₂ adsorption/desorption isotherms measurement with inset PSD profile of a porous sample. Reproduced with permission from ^[80]. Copyright © 2013. The Royal Society of Chemistry.

Figure 2.12 (a) XRD spectrums of the Mn_{0.1}Ni₁ electrodes calcined at 300 °C under various annealing durations (*e.g.* 0, 3, 19, and 15 h) and their corresponding (b) polarization curves of OER. (c) The surface area of the electrodes and OER current densities along the y-axis are plotted against different annealing periods (oxidation time). (a-c) Reproduced with permission from ^[86]. Copyright © 2015. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Figure 2.13 (a) Schematic synthesis of mesoporous MoS₂ consists of a DG morphology. (b) HRTEM image of the DG-MoS₂ consists of a pore size estimated to be 7 nm and [311] and [211] planes are being observed. (c) HER measurements of DG-MoS₂ in comparison with core-shell MoO₃-MoS₂ nanowires. (a-c) Reproduced with permission from ^[87]. Copyright © 2012. Nature Publishing Group.

Figure 2.14 (a) Synthetic approach for fabricating porous MoSe NSs. (b) Low-magnification TEM image displays porous MoSe₂ NSs. (c) LSV profiles consist of commercial Pt/C catalysts, nonporous MoSe₂ NSs and the porous MoSe₂ NSs.

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Figure 2.15 (a) Schematic illustration on the synthetic routes for making MoO₂ on PC and RGO. (b) HRTEM images of the MoO₂@PC-RGO sample. (c) LSV curves of MoO₂@PC versus MoO₂@PC-RGO in 0.5M H₂SO₄ solution. (a-c) Reproduced with permission from ^[90] Copyright © 2015. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Figure 2.16 Proposed mechanisms for hydrogen evolution reaction via hemolytic or heterolytic pathways. M represents the metallic electrocatalysts. Reproduced with permission from ^[95] Copyright © 2013. The Royal Society of Chemistry.

Figure 2.17 (a) ΔG_{H^*} versus the reaction coordinate. (b) ΔG_{H^*} diagram of various electrocatalysts (*e.g.* N-graphene, Pt, C₃N₄@NG, and g-C₃N₄@NG) for HER. (b) Reproduced with permission from ^[97]. Copyright © 2014. Nature Publishing Group. (c) The relationship between the logarithm of exchange current density ($\log i_0$) versus ΔG_{H^*} . (c) Reproduced with permission from ^[98] Copyright © 1958. Royal Society of Chemistry. (d) i_0 versus ΔG_{H^*} of various monometallic, non-metallic and composite materials. (d) Reproduced with permission from ^[97]. Copyright © 2014. Nature Publishing Group.

Figure 2.18 (a) The mixing of adsorbate and the metal energy levels. (a) Reproduced with permission from ^[100]. Copyright © 2005. Springer Link. (b) Schematic representation of the interaction between adsorbate orbital and

metal d band orbital, forming a bonding metal-adsorbate states (with a new d band) and an anti-bonding metal-adsorbate states. (b) Reproduced with permission from ^[101]. Copyright © 2010. The Royal Society of Chemistry. (c) Top: Experimental measurements of the occupied states and unoccupied states of N adsorbed on the Ni(100) and Cu(100) surface using XES and XAS, respectively. Bottom: Theoretical calculation of density of states of P_{xy} and P_z valence states of N adsorbed on Ni(100) and Cu(100) surface. Black line represents the occupied energy level (on the left side of Fermi level), while the gray line represents the unoccupied energy level (on the right side of Fermi level). (c) Reproduced with permission from ^[100]. Copyright © 2005. Springer Link. (d) Energy (ϵ) versus DOS of adsorbed H atom on the Ni(111), Cu(111), Pt(111) and Au(111) surface with arrows pointed at the anti-bonding of H 1s–d metal state. Unoccupied energy levels are represented in white and occupied energy levels are represented in gray. (d) Reproduced with permission from ^[102]. Copyright © 1995. Nature Publishing Group.

Figure 2.19 ΔG_{H^*} versus $E_d - E_F$. All the values of ΔG_{H^*} are taken from reference ^[103] and the values for $E_d - E_F$ are taken from reference ^[104].

Figure 2.20 Molecular orbital bonding of σ donation (*e.g.* $M \leftarrow H_2$) and π back donation (*e.g.* $M \rightarrow H_2$). Reproduced with permission from ^[105]. Copyright © 2009. The Royal Society of Chemistry.

Figure 3.1 (a) Schematic illustration of the basic components in SEM and (b) TEM. Figure 3.1 (a-b) obtained from reference ^[28].

Figure 3.2 (a) Schematic illustration of AFM components. Reproduced with permission from ^[30]. Copyright © 2011. (a) The Royal Society of Chemistry. (b) AFM image and (c) height profile of a 2D material.

Figure 3.3 (a) Schematic illustration of the typical constituents in the XRD machine. Figure 3.3a obtained from reference ^[31]. (b) Schematic representation of Bragg diffraction. Figure 3.3b obtained from reference ^[29]. (c) XRD pattern of tungsten (W) substrate.

Figure 3.4 (a) Schematic representation of the main components in the XPS instrument. (a) Reproduced with permission from ^[32] Copyright © 2011. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Mechanism of photoelectron spectroscopy. (c) Typical XPS spectrum.

Figure 3.5 (a) Schematic representation of the main components in the ICP-OES instrument. (b) Processes occur during high-temperature heating of the sample solution. (c) Linear calibration plot of various standard concentrations is used to determine concentration in the sample. (a-c) Reproduced with permission from ^[34] Copyright © 1997. Perkin-Elmer.

Figure 3.6 (a) Schematic representation of the major components in the NMR instrument. (b) Processes take place in NMR instrument. (c) The FID signal is converted to the frequency chart via Fourier transform. (d) The typical range of ¹³C and ¹H chemical shifts for C and H atoms with various neighboring atoms. Figure 3.6 (a-d) obtained from reference ^[35].

Figure 3.7 (a) Schematic representation of the main components of BET instrument. (b) Schematic representation of the monolayer adsorption represents Langmuir theory and multilayer adsorption represents BET theory. (c) Five types of adsorption isotherms. (c) Reproduced with permission from ^[37]. Copyright © 1940. American Chemical Society.

Figure 3.8 (a) Schematic illustration of the of the major components in contact angle instrument. (b) Image of different samples with contact angles of 41° and

(c) 110° . (a-c) Reproduced with permission from ^[38]. Copyright © 2010. American Chemical Society.

Figure 3.9 (a) Schematic illustration of the typical 2-electrode and 3-electrode systems consist of W.E, C.E, R.E, and electrolyte. (b) A typical LSV curve for HER. (c) CV curves performed at various scan rates. (d) Current density difference at 0.25 V *versus* RHE plotted against various scan rates based on Figure 3.9c. (e) A typical Nyquist plot and (f) voltage versus capacity profile for Li-O₂ battery.

Figure 4.1 (a) TEM images of various cathodes (*e.g.* Pt NWs, IrO₂/Pt NWs, and CuO/Pt NWs) measured during discharging and charging of Li-O₂ battery. (b) Contact angle measurement of Pt NWs, IrO₂/Pt NWs, and CuO/Pt NWs samples on stainless steel foil. (c) Proposed interaction between adsorbates (*e.g.* Li₂O₂ and H₂O) and substrates (*e.g.* Pt NWs, IrO₂/Pt NWs, and CuO/Pt NWs).

Figure 4.2 (a) XPS spectrums of (i) IrO₂/Pt NWs and (ii) CuO/Pt NWs. (b) TEM images with FFT of (i) IrO₂/Pt NWs and (ii) CuO/Pt NWs. (c) Crystal structure representations of (i) IrO₂/Pt NWs with (110)-oriented and (ii) CuO/Pt NWs with (002)-oriented.

Figure 4.3 Simple schematic illustration of the interactions between adsorbates and substrates. The chemical bond lengths are not drawn to scale. (a) Li₂O₂ layer on MO surface; (b) Li₂O₂ NPs on Pt surface; (c) H₂O molecules wet on MO surface; (d) H₂O molecules do not wet well on Pt surface.

Figure 4.4 (a) Voltage versus capacity profiles for Li-O₂ batteries with Pt NWs, CuO/Pt NWs, and IrO₂/Pt NWs samples at 100 mA g⁻¹. (b) Proposed mechanisms of Li₂O₂ thin layer and Li₂O₂ NPs formation in MO/Pt and Pt batteries, respectively.

Figure 4.5 Simple representation of a multi-step growth mechanism of the CuO/Pt NSs on SSM.

Figure 4.6 (a) Top view and (b) side view SEM images of Pt NSs grown on SSM. (c) Low-magnified TEM image and (d) enlarged TEM image includes EDX line scan graphs of CuO/Pt NSs sample where red line represents Pt and blue line represents Fe (e) SEM image with inset PSD profile of CuO/Pt NSs grown on SSM. (f) HRTEM image and (g) SAED pattern of CuO/Pt NSs where red circle represents Pt and blue circle represents Fe

Figure 4.7 (a) Low magnified SEM image related to porous Pt NSs grown on SSM. (b) HRTEM image of the Fe root protruding out of Pt NSs.

Figure 4.8 XRD patterns of the SSM (bottom, black), Pt NSs on SSM (center, red), and CuO/Pt NSs on SSM (top, blue).

Figure 4.9 SEM images of (a) the smooth SSM and (b) SSM undergoes thermal decomposition. (c) Point EDX analysis marked by black dotted line shows the elemental composition of the smooth SSM surface. (d) Fe seeds are marked by red dotted circle with its corresponding point EDX analysis (marked with red dotted line) shows the presence of elemental Fe.

Figure 4.10 SEM image of (a) Si/SiO₂ substrate and (b) thermal deposition of Pt growth solution with Si/SiO₂ substrate in quartz tube furnace.

Figure 4.11 EDX spectrum of CuO/Pt NSs hybrid.

Figure 4.12 (a) HAADF-STEM image and (b-d) elemental mapping images of CuO/Pt NSs. (e) Cu 2p spectrum and (f) Pt 4f spectrum of the CuO/Pt NSs sample.

Figure 4.13 (a-b) Low-magnified SEM images of CuO/Pt NSs and (c) nanoparticles size distribution

Figure 4.14 N₂ desorption/adsorption isotherms of the samples and bare stainless steel.

Figure 4.15 (a) Voltage versus capacity profile of Li-O₂ batteries at 1 A g⁻¹ consists of Pt NSs and CuO/Pt NSs electrodes. (b) Proposed mechanisms of Li₂O₂ NPs and Li₂O₂ thin layer formation in Pt NSs and CuO/Pt NSs batteries, respectively. SEM images of (c) discharged and (d) charged Pt NSs cathode. SEM images of (e) discharged and (f) charged the CuO/Pt NSs cathode

Figure 4.16 XPS Li 1s spectrums of discharged cathode and charged cathode of (a) Pt NSs and (b) CuO/Pt NSs.

Figure 4.17 (a) Voltage versus capacity profile of Li-O₂ batteries at 100 mA g⁻¹, 500 mA g⁻¹, 1 A g⁻¹ (1st cycle) and 1 A g⁻¹ (60th cycle) for Li-O₂ batteries with CuO/Pt NSs. (b) Voltage versus capacity profile of Li-O₂ batteries at 100 mA g⁻¹, 500 mA g⁻¹, 1 A g⁻¹ (1st cycle) and 1 A g⁻¹ (60th cycle) for Li-O₂ batteries with Pt NSs. (c) Charging voltage and specific capacity plot along y-axis against cycle number at 1 A g⁻¹ for CuO/Pt NSs battery. (d) Charging voltage and specific capacity plot along y-axis versus cycle life at 1 A g⁻¹ for Pt NSs battery.

Figure 4.18 Nyquist plot of Pt NSs and CuO/Pt NSs batteries at 1st full discharge under 1 atmospheric pressure O₂.

Figure 4.19 ¹H NMR spectrums of (a-b) Pt NSs and (c-d) CuO/Pt NSs batteries at discharged and charged states.

Figure 5.1 Simple representation of growth processes of 3DHP-Mo₂C. (I): Solvothermal treatment of a mixture containing pyridine and sodium (Na) to obtained PNDCF. (II): Evaporation of the aqueous mixture (containing Mo and

PND CF precursors) to obtain Mo-PND CF hybrid. (III): Carburization of Mo-PND CF hybrid to form 3DHP-Mo₂C product.

Figure 5.2 (a) XRD pattern, (b) low-magnified SEM image, (c) high-magnified SEM image, (d) TEM image, (e) HRTEM image, (f) HAADF-STEM image, and elemental mappings of 3DHP-Mo₂C sample.

Figure 5.3 XRD patterns of (a) I-Mo₂C/NCNT, (b) I-Mo₂C/CNT, and (c) PND CF samples.

Figure 5.4 XPS N 1s spectrums of (a) 3DHP-Mo₂C and (b) I-Mo₂C/NCNT samples.

Figure 5.5 (a) SEM image and (b) TEM image of PND CF sample.

Figure 5.6 SEM images of (a-b) I-Mo₂C/CNT and (c-d) I-Mo₂C/NCNT samples.

Figure 5.7 TEM and HRTEM images of (a-c) I-Mo₂C/CNT and (d-f) I-Mo₂C/NCNT.

Figure 5.8 HAADF images and EDX elemental mapping images of (a-c) I-Mo₂C/CNT and (d-g) I-Mo₂C/NCNT samples.

Figure 5.9 (a) N₂ desorption-adsorption isotherm, (b) PSD, and (c) CPV profiles of the 3DHP-Mo₂C sample.

Figure 5.10 (a) N₂ adsorption and desorption isotherm, (d) PSD, and (g) CPV profiles of I-Mo₂C/CNT (b) N₂ adsorption and desorption isotherm, (e) PSD, and (h) CPV profiles of I-Mo₂C/NCNT. (c) N₂ adsorption and desorption isotherm, (f) PSD, and (i) CPV profiles of PND CF.

Figure 5.11 Polarization curves of 3DHP-Mo₂C electrocatalyst with various Mo₂C *wt%* loading on the PND CF support in 0.5 M H₂SO₄ solution. The content of Mo₂C *wt%* on the PND CF support was determined using ICP-OES elemental analysis (see details in Calculation A.2).

Figure 5.12 (a) Polarization curves of I-Mo₂C/CNT, I-Mo₂C/NCNT, 3DHP-Mo₂C, carbon supports (CNT, NCNT and PND CF), and Pt/C electrocatalysts at 2 mV s⁻¹ in 0.5 M H₂SO₄. (b) Tafel plots of I-Mo₂C/CNT, I-Mo₂C/NCNT, 3DHP-Mo₂C, and Pt/C samples. (c) Schematic representation of the polarization (η) between microporous and mesoporous materials. (d) Schematic representation of the proton mass transport in microporous and mesoporous materials.

Figure 5.13 CV measurements at a range from 0.04–0.44 *versus* RHE without faradic processes. A series of CV measurements were performed at various scan rates of 5, 10, 20, 50, and 100 mV s⁻¹ for (a) 3DHP-Mo₂C, (b) I-Mo₂C/NCNT and (c) I-Mo₂C/CNT samples. (d) Current density difference ($i_a - i_c$, defined at 0.25 V *versus* RHE) as a function of different scan rates for these electrocatalysts.

Figure 5.14 TOF of the electrocatalysts are derived from (a) specific surface area (based on BET model) is named TOF_{BET} (see details in Calculation A.3) and (b) RF is named as TOF_{RF} (see details in Calculation A.4).

Figure 5.15 (a) Nyquist plots collected on 3DHP-Mo₂C at various overpotentials. (b) Nyquist plots of the I-Mo₂C/CNT, I-Mo₂C/NCNT and 3DHP-Mo₂C recorded at $\eta = 200$ mV in 0.5 M H₂SO₄ solution with inset of Randles circuit model (R_s represents series resistance consists of resistance in wiring, resistance of electrode and solution resistance; R_{ct} denoted as the charge transfer resistance; C_{dl} denoted as double-layer capacitance).

Figure 5.16 Durability test of hierarchical 3DHP-Mo₂C consists of polarization curves at 2 mV s^{-1} and time-dependant current density curve under $\eta = 100$ mV for 28 h in (a-b) pH 0, (c-d) pH 7 and (e-f) pH 14 media.

Figure 5.17 TEM images and SAED patterns of 3DHP-Mo₂C electrocatalyst after being HER electrocatalyzed for 28 h in (a-d) pH 0, (e-h) pH 7 and (i-l) pH 14 solutions.

Figure 5.18 Faraday efficiency of hydrogen generation over 3DHP-Mo₂C at 25 mA cm^{-2} measured for 240 min at (a-b) pH 0, (c-d) pH 7 and (e-f) pH 14 media. See details in Calculation A.5.

Figure 6.1 Schematic illustration of the growth processes of chemically doped Mo₂C NSs.

Figure 6.2 (a) XRD patterns, (b) XPS Mo 3p and N 1s spectrum, and (c) XPS S 2p spectrum of Mo₂C and N/S-doped Mo₂C samples. (d-e) Low-magnified TEM images of Mo₂C and N/S-doped Mo₂C NSs, respectively. High magnified TEM images include SAED image of (f) Mo₂C and (g) N/S-doped Mo₂C. AFM images with inset height profile of (h) Mo₂C and (i) N/S-doped Mo₂C samples.

Figure 6.3 (a) XRD patterns, (b) XPS Mo 3p and N 1s spectrum, and (c) XPS S 2p spectrum of S-doped Mo₂C and N-doped Mo₂C samples. Low-magnified TEM images of (d) S-doped Mo₂C and (e) N-doped Mo₂C samples. High magnified TEM images with inset SAED pattern of (f) S-doped Mo₂C and (g) N-doped Mo₂C. AFM images with inset height profile of (h) S-doped Mo₂C and (i) N-doped Mo₂C samples.

Figure 6.4 (a) Large-area AFM image and (b) low-magnification TEM image of N/S-doped Mo₂C NSs.

Figure 6.5 Nitrogen adsorption/desorption isotherms of Mo₂C NSs samples. (a) Mo₂C, (b) S-doped Mo₂C, (c) N-doped Mo₂C and (d) N/S-doped Mo₂C.

Figure 6.6 HAADF images and their corresponding EDX mapping images of (a-d) S-doped Mo₂C, (e-h) N-doped Mo₂C and (i-m) N/S-doped Mo₂C samples.

Figure 6.7 Contact angle of the Mo₂C and N/S-doped Mo₂C samples was taken a various time.

Figure 6.8 Contact angle of the S-doped Mo₂C and N-doped Mo₂C samples was taken a various time.

Figure 6.9 Polarization curves for layered bulk Mo₂C and Mo₂C samples in 0.5 M H₂SO₄ at 2 mV s⁻¹.

Figure 6.10 (a) LSV curves, (b) Tafel plots, (c-d) durability test of Mo₂C, S-doped Mo₂C, N-doped Mo₂C, N, S-doped Mo₂C and Pt/C samples in 0.5 M H₂SO₄ at 2 mV s⁻¹. The TEM image and SAED pattern of N/S-doped Mo₂C sample after stability test.

Figure 6.11 EIS analysis of fitted (a) Nyquist plot of N/S-doped Mo₂C sample in 0.5 M H₂SO₄ at various overpotentials and (b) EIS of Mo₂C samples at 200 mV in 0.5 M H₂SO₄ solution.

Figure 6.12 (a) Proposed catalytic cycle for HER. (b) Synergistic effect of N/S doped Mo₂C. (c) HOMO of S→Mo⁽ⁿ⁾L_n complex π back donation to LUMO of H₃O⁺. The energy levels of the molecular orbitals of H₃O⁺ are taken from reference [27].

Figure 7.1 (a) Schematic illustration of a 3-electrode photocatalytic Li-O₂ battery consists of Li anode, carbon cathode for discharging, and dye-sensitized TiO₂ photoelectrode for charging process. (b) Charging voltage profile of photocatalytic Li-O₂ battery with dye-sensitized TiO₂ electrode. (a-b) Reproduced with permission from [5]. Copyright © 2014. Nature Publishing Group. (c) Schematic representation of a 2-electrode system consists of Li anode and C₃N₄ grown on carbon paper. (d) Discharging/charging voltage profile of photocatalytic Li-O₂ battery with C₃N₄. (c-d) Reproduced with permission from [6]. Copyright © 2015. The Royal Society of Chemistry.

Figure 7.2 (a) Schematic representation of the proposed mechanism for photocatalytic charging process in the photocatalytic Li-O₂ battery with dye-sensitized TiO₂ photoelectrode. (a) Reproduced with permission from [5]. Copyright © 2014. Nature Publishing Group. (b) Schematic illustration of the proposed mechanism for photocatalytic charging process in the photocatalytic Li-O₂ battery with C₃N₄ photoelectrode. (b) Reproduced with permission from [6]. Copyright © 2015. The Royal Society of Chemistry.

Figure 7.3 (a) Schematic diagram illustrating the growth processes for M-doped (M: Fe, Co, Ni) W₂C nanosheets arrays (NSAs) on tungsten (W) substrate. (b) LSV curve of W substrate and (c) LSV profiles of the Pt/C, W₂C, Fe-doped W₂C,

Co-doped W₂C, and Ni-doped W₂C NSAs at 2 mV s⁻¹ in 0.5 M H₂SO₄ (pH 0) solution.

Figure 7.4 (a) The calculated free energy (ΔG_{H^*}) diagram of the M-doped W₂C surface (M: Fe, Co, Ni) and pure W₂C models for HER at equilibrium potential ($U_{RHE} = 0$ V). (b) Volcano plots of i_o in logarithm scale versus free ΔG_{H^*} values of electrocatalysts reported in the literature and in this work (data collected from references is summarized in Table A.9).

Figure A.1 3D schematic representation of the simulated (a) unit cell and b) crystal structure of β -Mo₂C phase with an ABABAB stacking sequences consists of hexagonal structure and space group of P63/mmc with (101)-oriented in c direction.

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Calculation Captions

Calculation A.1: Determination of total specific capacities

Calculation A.2: Determination the Mo₂C loading in Mo₂C/Csupport sample using ICP-OES and CHNS analyses

Calculation A.3: Determination of TOF_{BET}

Calculation A.4: Determination of TOF_{RF}

Calculation A.5: Determination of Faraday efficiency

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Abbreviations

AC	Alternating Current
AFM	Atomic Force Microscopy
BET	Brunauer-Emmett-Teller
BE	Binding Energy
BF	Bright Field
BJH	Barrett-Joyner-Halenda
BSE	Backscattered Electron
CA	Contact Angle
CB	Conduction Band
C.E	Counter Electrode
CHNS	Carbon Hydrogen Nitrogen Sulfur
CNT	Carbon NanoTube
CPV	Cumulative Pore Volume
CRT	Cathode-Ray Tube
CUS	Coordinative Unsaturated Sites
CV	Cyclic Voltammetry
DF	Dark Field
DFT	Density Functional Theory
DG	Double-Gyroid
DOS	Density of One-electron State
EDX	Energy Dispersive X-ray
EIS	Electrochemical Impedance Spectroscopy
ECSA	ElectroChemical Surface Area
FESEM	Field Emission Scanning Electron Microscopy
FFT	Fast Fourier Transform
FID	Free-Induction Decay
HAADF	High-Angle Annular Dark-Field
HER	Hydrogen Evolution Reaction
HOMO	Highest Occupied Molecular Orbital

HOR	Hydrogen Oxidation Reaction
HR	High-Resolution
HTC	HydroThermal Carbonization
ICP-OES	Inductively Coupled Plasma–Optical Emission Spectroscopy
KE	Kinetic Energy
LBE	Long Boundary End
LSV	Linear Sweep Voltammetry
LUMO	Lowest Unoccupied Molecular Orbital
MO	Metal Oxide
MOF	Metal-Organic Framework
NHE	Normal Hydrogen Electrode
NCNT	Nitrogen-doped Carbon NanoTube
NG	Nitrogen-doped Graphene
NMR	Nuclear Magnetic Resonance
NP	NanoParticle
NS	NanoSheet
N/S	Nitrogen-Sulfur
NSA	NanoSheet Array
NR	NanoRod
NW	NanoWire
OCV	Open Circuit Voltage
OPV	Organic PhotoVoltaic
OER	Oxygen Evolution Reaction
ORR	Oxygen Reduction Reaction
PC	Porous Carbon
PPM	Parts Per Million
PMT	PhotoMultiplier Tube
PND CF	Porous Nitrogen-Doped Carbon Framework
POM	PolyOxoMetalate
PS	Pressure Saturated

PSA	Pore Size Distribution
R.E	Reference Electrode
RF	Roughness Factor
RGO	Reduced Graphene Oxide
RDF	RaDio Frequency
RHE	Reversible Hydrogen Electrode
SAED	Selected Area Electron Diffraction
SBE	Short Boundary End
SCE	Saturated Calomel Electrode
SE	Secondary Electron
SEM	Scanning Electron Microscopy
SSA	Specific Surface Area
SSM	Stainless Steel Mesh
STEM	Scanning Transmission Electron Microscopy
TEGDME	TetraEthylene Glycol DiMethyl Ether
TEM	Transmission Electron Microscopy
TMBE	Transition-Metal Based Electrocatalyst
TOF	TurnOver Frequency
W.E	Working Electrode
XAS	X-ray Absorption Spectroscopy
XES	X-ray Emission Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
VB	Valence Band
0D	Zero-Dimensional
1D	One-Dimensional
2D	Two-Dimensional
3D	Three-Dimensional
3DHP	Three-Dimensional Hierarchical Porous

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Major Symbols

<u>Symbol</u>	<u>Meaning</u>
α	transfer coefficient
C_{dl}	double-layer capacitance
$C_{O(0,t)}$	concentration of oxidize species at time=0 to finite time(t)
$C_{R(0,t)}$	concentration of reduce species at time=0 to finite time(t)
C_O^*	bulk concentration of oxidize species
C_R^*	bulk concentration of reduce species
ρ	density of scattering atom
δ	chemical shift
ΔE_{cell}	difference in standard potential for cell reaction
$\Delta E_{applied}$	difference in applied potential
E_d	d-band energy
E_F	Fermi energy
F	Faraday's constant
γ	surface free energy
$\Delta G^\ddagger$	change in Gibbs free energy of reaction
$\Delta G_F^\ddagger$	change in Gibbs free energy of forward reaction
$\Delta G_B^\ddagger$	change in Gibbs free energy of backward reaction
ΔG_{H^*}	change in Gibbs free energy of hydrogen adsorption
ΔG_{rxn}	change in the Gibbs free energy of activation
H^*	hydrogen-catalyst intermediate
h	Planck's constant
ΔH_{rxn}	change in enthalpy of reaction
i_a	anodic current
i_c	cathodic current
i_o	exchange current
j	current density

k_B	Boltzmann constant
k_{FW}	rate constant of forward reaction
k_{BW}	rate constant of backward reaction
λ	wavelength
M	molar mass
N_A	Avogadro's number
η	overpotential in general
η_{CT}	charge transfer overpotential
η_D	diffusion overpotential
η_o	ohmic polarization
θ	contact angle or diffraction angle
P_{O_2}	partial pressure of oxygen
π	metal to ligand ($M \rightarrow L$) pi back donation
ΔS_{rxn}	change in entropy of reaction
σ	ligand to metal ($L \rightarrow M$) sigma donation
σ_{atom}	effective radius of single atom
R	gas constant
R_s	ohmic resistance
R_{CT}	charge transfer resistance
T	reaction temperature
T_{abs}	absolute temperature
U_{RHE}	equilibrium potential
ν	frequency of electromagnetic radiation
v_{FW}	rate of forward reaction
v_{BW}	rate of backward reaction
W_J	joulic heat
W_K	thermal heat
X_o	molar fraction of oxygen dissolved in metal oxide
z	number of electrons involve in the cell reaction

Chapter 1

Introduction

In this chapter, the problem statements, propose hypotheses, design and performance targets of the thesis will be discussed. Next, the objective and the scope regarding the rational-design of transition-metal based electrocatalysts (TMBE) for high energy storage devices will be presented. Following on, the dissertation overview of individual chapters will be briefly conferred. Lastly, the progresses and novelty of the research will be summarized in the findings and outcomes/originality section.

1.1 Problem statements/Hypotheses/Design and performance targets

In recent years, high energy storage devices (*e.g.* Li-O₂ batteries and hydrogen fuel cell) have been accentuated by researchers due to their high theoretical specific energy over the commercial Lithium-ion batteries. ^[1-5] These applications, however, still encounter one major challenge, which is the slow reaction kinetics that cause large overpotential and in turn leads to energy losses in these high energy storage devices. ^[6-10] Therefore, rational-design of electrocatalysts becomes vital for the improvement of the reaction kinetics and facilitates in maximizing the energy output over the energy input for high energy storage devices. In this research, we are focusing on the lowering of activation overpotential and enhancing the energy efficiency by tuning the transition-metal based electrocatalysts (TMBE) properties such as: (1) improving the wetting property of the TMBE by introducing metal oxide (*e.g.* IrO₂ or CuO) on noble metal (*e.g.* Pt) to “wet” the Li₂O₂ molecule when Li-O₂ battery is being discharged; (2) speeding up the proton diffusion rate in hydrogen evolution reaction (HER) by designing a TMBE that consists of dominant micropores (*e.g.* microporous Mo₂C); (3) providing synergistic effect by co-doping heteroatoms (*e.g.* nitrogen and sulfur) into TMBE (*e.g.* Mo₂C) in order to optimize the metal-adsorbate electronic structure for HER.

Problem statement #1:

How does the wetting property of the TMBE influence the oxygen evolution reaction (OER) in Li-O₂ battery?

Hypothesis #1:

In the case of wetting property, TMBE that made up of metal oxide (MO) exhibits better “wetting” affinity towards Li₂O₂ molecules as compared to non-metal oxide material. As a result, the former promotes the formation of thin layer of Li₂O₂ product during discharging of Li-O₂ battery. This Li₂O₂ thin layer provides a short electron transport pathway, and thus improves the reaction kinetics for OER during the charging process.

Design/Performance Target #1:

In Chapter 4, we deposited MO (*e.g.* IrO_2 or CuO) onto Pt electrode to improve the “wetting” affinity of TMBE towards Li_2O_2 molecule, forming Li_2O_2 thin layer during discharging of Li- O_2 battery. For instance, the Li- O_2 battery with CuO/Pt nanosheets (NSs) growing on the stainless steel mesh (SSM) has a charging voltage of 3.51 V *versus* Li^+/Li , which is smaller than that of the Li- O_2 battery with Pt NSs growing on SSM (4.45 V *versus* Li^+/Li) as defined at the specific capacity of 400 mAh g^{-1} .

Problem statement #2:

Why does the microporous TMBE have a better reaction kinetics as compared to mesoporous TMBE in the HER?

Hypothesis #2:

Micropores in TMBE facilitate fast proton mass transport in HER as compared to mesopores in TMBE. The former boosts the HER kinetics, leading to a lower HER overpotential.

Design/Performance Target #2:

In Chapter 5, we have fabricated microporous Mo_2C in comparison with mesoporous Mo_2C for HER. For example, three-dimensional hierarchical porous (3DHP) Mo_2C with dominant micropores displays a 97 mV operating HER overpotential, which is below the operation HER overpotential of the interweaved $\text{Mo}_2\text{C}/\text{carbon nanotube}$ (I- $\text{Mo}_2\text{C}/\text{CNT}$) with dominant mesopores (148 mV) as defined at a practical current density of 10 mA cm^{-2} .

Problem statement #3:

How does co-doping of heteroatoms into TMBE change the catalyst-adsorbate electronic structure for efficient HER?

Hypothesis #3:

Chemical co-doping of heteroatoms into TMBE lattice could alter the electronic structure of catalyst-adsorbate species and changes the interaction between the

catalyst and adsorbate. According to Sabatier principle, an ideal catalyst consists of a moderate catalyst-adsorbate interaction. The catalytic active sites will be blocked if the catalyst-adsorbate interaction is too strong, whereas the reaction will not occur if the catalyst-adsorbate interaction is too weak.

Design/Performance Target #3:

In Chapter 6, we have synthesized nitrogen-sulfur (N/S) co-doped Mo₂C in comparison with singly doped Mo₂C (*e.g.* S-doped Mo₂C and N-doped Mo₂C), and pure Mo₂C. The N, S-doped Mo₂C electrocatalyst shows a 46 mV onset potential, which is lesser than the other electrocatalysts. For example, the onset potentials for N-doped Mo₂C, S-doped Mo₂C, and Mo₂C samples are 186 mV and 144 mV, and 234 mV, respectively.

1.2 Objective and scope

The ultimate goal of this thesis is to curtail the overpotential in electrocatalysis in order to maximize the energy efficiency and minimize energy losses by rational-design of electrocatalysts through the scope as follows:

1. Improving the wetting property of the TMBE by deposition of metal oxide onto noble metal electrode for Li-O₂ battery;
2. Speeding up the proton diffusion rate by fabricating TMBE that consists of dominant micropores for HER;
3. Introducing synergistic effect by heteroatoms co-doping (*e.g.* N and S) into the TMBE lattice for HER.

1.3 Dissertation overview

The thesis addresses the development of various strategies for fabricating novel TMBEs together with their intrinsic properties (*e.g.* wetting, porosity and metal-adsorbate electronic structure) in order to obtain a great energy efficacy for high energy storage devices (*e.g.* Li-O₂ battery and hydrogen fuel cell). In total, 7 chapters are discussed and arranged in a manner as follows:

Chapter 1 defines the problem statements, proposes the hypotheses and performance targets for this study; summarizes the objective and scope for this research; presents the findings and outcomes/originality of this work.

Chapter 2 reviews the literatures, which addressed the importance, mechanisms and challenges for high energy storage devices (*e.g.* Li-O₂ battery and hydrogen fuel cell); discusses the kinetics limitations for electrocatalysis. It also provides the readers with knowledge on the topics (*e.g.* wetting, porosity, and metal-adsorbate electronic structure) that are related to this research. Lastly, it raises a short question to discuss and answer the PhD in the context based on the literature findings.

Chapter 3 discusses the rationale for selection of materials/methods and elaborates the principles of synthesis/characterization techniques used in this context. Also, it discusses the limitations of each characterization techniques.

Chapter 4 elaborates on the “wetting” affinity between MO and Li₂O₂ molecules during discharging of Li-O₂ battery.

Chapter 5 elaborates on the effects of pore size for HER.

Chapter 6 elaborates on the catalyst-adsorbate electronic structure for HER.

Chapter 7 discusses the threads, implications and impacts of the thesis. It addresses whether the hypothesis of each study has been proven, or the design target has been met. Lastly, it includes the reconnaissance studies and outstanding questions raised relating to the future work.

1.4 Major findings and outcomes/originality

This research led to several novel outcomes:

1. Introduce MO (*e.g.* CuO) on the Pt NSs could improve the interaction between Li_2O_2 molecules and MO on electrode surface (*e.g.* CuO/Pt NSs grown on SSM). This interaction “wets” the Li_2O_2 molecules on MO surface, forming Li_2O_2 thin layer during discharging of Li-O₂ battery. Li_2O_2 thin layer provides a short electron transport pathway for OER during charging process. Therefore, when the current density is 1 A g^{-1} , a lower charging voltage of 3.73 V is being reported. Heretofore the ultra-low charging voltage with great rate capability is the best record for the carbon-free Li-O₂ battery.
2. For the first time, we observe that the micropores in the TMBE (*e.g.* 3DHP-Mo₂C) are very vital for efficient HER. It reduces the energy barrier pathway for proton mass transport, which enhances the HER kinetics in comparison with the mesoporous TMBE (*e.g.* I-Mo₂C/CNT). Such microporous 3DHP-Mo₂C exhibits a low onset potential of 37 mV, which is the best that has ever been reported for noble-metal free HER.
3. We modify the electronic structure of Mo₂C materials by chemically co-doped with non-metal atoms (*e.g.* N and S). The N (act as electron acceptor) and S (act as electron donor) non-metal atoms in the Mo complex improve the adsorption strength of catalyst-adsorbate (via σ -donation) and increase the H₂ production (via π -back donation), respectively. In addition, our density functional theory results are in accordance with the experimental HER results. These lead to an extraordinary small HER operating potential of -86 mV at 10 mA cm^{-2} is obtained.

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Chapter 2

Literature Review

In this chapter, an analysis on the importance, mechanisms and challenges for high energy storage devices (e.g. Li-O₂ battery and hydrogen production) is presented. Following on, the kinetics limitation for electrocatalysis is discussed. This chapter provides readers with knowledge on topics (e.g. wetting, porosity, and metal-adsorbate electronic structure) that are related to this study. Lastly, the question to discuss and answer the PhD in context based on literature will be presented.

2.1 Overview

As traditional sources of energy, the consumption of the scarce fossil fuels is responsible for the huge amount of carbon dioxide generated and is one of the primary causes of global warming. Therefore, the technological development of sustainable energy has become utterly imperative.^[1-3] However, there is still a great challenge to replace fossil fuels by renewable energy entirely, which enables users to store electrical energy efficiently on a large scale and use it efficiently whenever it is needed. Electrocatalysis is an electrochemical reaction process involves the use of an electrocatalyst, which provides a less energy demanding pathway to store electrical energy more efficiently in the chemical bonds.^[4] For instance, we can split metal oxide (*e.g.* M_xO_y where M: Li, Na, Zn, Al) into energy carriers (*e.g.* oxygen molecule and metal) in metal oxygen batteries.^[5-8] Alternatively, we can split a water molecule into energy carriers (*e.g.* oxygen molecule and hydrogen molecule) in electrolyzes.^[9]

Figure 2.1 Ragone plot (x-axis: specific energy versus y-axis: specific power) of various energy storage devices. The Ragone plot is reproduced from reference [Atsushi, Tsutsumi. “Fuel Cell/Battery System.” *UTokyo Research*. The University of Tokyo, 13 August 2013 Published. <http://www.u-tokyo.ac.jp/en/utokyo-research/editors-choice/fuel-cellbattery-system/> 1 June 2016 Accessed.]^[10] Copyright Atsushi Tsutsumi.

Currently, metal-air battery and hydrogen fuel have become popular research subjects because of their high specific energy range of $10^2 - 10^4$ Wh/kg, which is undoubtedly greater than the commercial Lithium-ion batteries in the market ($10^1 - 10^2$ Wh/kg).^[10-12] Figure 2.1 illustrates disparate energy storage devices with specific energy plotted along x-axis against the specific power at the y-axis. This plot is known as the Ragone plot. The specific energy indicates the duration of the usage (*e.g.* the larger the specific energy value, the longer the usage) whilst the specific power shows the rate of charging/discharging (*e.g.* the larger the specific power value, the faster the charging process). Among all the energy storage devices, the ones that involve electrocatalysis are metal-air batteries and fuel cells, which possess much higher specific energy as compared to the rest of the devices. Unfortunately, majority of energy losses in these two systems are related to the slow reaction kinetics of their respective electrochemical reactions, leading to a large overpotential polarization and therefore reduce their energy efficiency.^[13-14] Hence, the energy inefficiency compromises the key advantage of their high specific energy.

Figure 2.2 (a) Storage and conversion mechanisms for a non-aqueous Li-O₂ battery. (b) Schematic illustration on the thermodynamic potential of OER/ORR: $2\text{Li}^+ + 2\text{e}^- + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2$ is ~0 V *versus* NHE (equivalent to 2.96 V *versus* Li^+/Li). (c) During discharging, Li^+ ions from the anode undergo reduction with O_2 molecules from the cathode, forming Li_2O_2 on the cathode and this process is called ORR. (d) During charging, the Li_2O_2 on the cathode surface undergoes OER, forming Li^+ ions and O_2 molecules.

For the past few decades, the rechargeable Li-O₂ batteries have gained more interests as they have a high theoretical specific energy of ~3560 W h kg⁻¹.^[15] The energy storage mechanism in the Li-O₂ battery is established by the splitting of the Li₂O₂ into energy carriers (*e.g.* O₂ and Li). In the reverse process for energy conversion, Li and O₂ recombine to form Li₂O₂, producing energy for consumption (Figure 2.2a). The thermodynamic value for reduction /oxidation reactions of lithium peroxide ($2\text{Li}^+ + 2\text{e}^- + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2$) is defined at 2.96 V *versus* Li⁺/Li (0 V *versus* NHE), as illustrated in Figure 2.2b. During discharging of the Li-O₂ battery, the Li⁺ ions and O₂ molecules undergo the oxygen reduction reaction (ORR) and form Li₂O₂ on the oxygen cathode (Figure 2.2c). During charging, the Li₂O₂ on the electrode surface undergoes the oxygen evolution reaction (OER) and converts Li₂O₂ back to Li⁺ ions and O₂ molecules (Figure 2.2d). The greatest challenge for the Li-O₂ cell is that there is a huge amount of energy losses arising from large polarization, which deviates from the thermodynamical potential of 2.96 V *versus* Li⁺/Li reference.^[16] During ORR reaction, the insulating Li₂O₂ precipitated on the electrode surface often leads to sluggish OER kinetics, resulting in a high charging voltage.^[17] In addition, the highly reactive reduced peroxide (O₂²⁻) at the cathode-electrolyte interface attacks the carbon-based cathode and aprotic solvent, causing the formation of the irreversible parasitic products (*e.g.* CH₃CO₂Li, HCO₂Li, and Li₂CO₃).^[18-19] The decomposition of these undesired side reactions consumes extra energy at higher polarization during charging and the accumulation of these interfacial layers will degrade the cycle life of the Li-O₂ batteries. The carbon-based cathode drives the OER overpotential above 4 V_{Li/Li}⁺ due to the formation of parasitic products.^[20] These highly unstable carbon-based cathodes^[18, 21-22] and non-aqueous electrolytes^[19, 23-24] have constrained the performance of the Li-O₂ batteries to a low cycle life (<10 cycles), poor round-trip efficiency (<75%) and a low rate capability.^[16] Despite these sophisticated Li-O₂ systems, many researchers have been motivated in exploring new systems for highly rechargeable Li-O₂ batteries. For example, numerous research groups have been

working on ORR and OER reactions, which consist of carbon [20-21, 25-28], non-noble metal, [29-33] and noble metal [30, 34-38] materials. It is also known that the structures of the catalysts have various effects on the electrocatalytic activities, which influence the electrochemical performance within the Li-O₂ batteries. [32, 39] For instance, zero-dimensional (0D) nanostructure has the particle to particle interfacial resistance, which obstructs the electron transfer. One-dimensional (1D) and two-dimensional (2D) nanostructures offer continuous and facile electron transport pathways. Three-dimensional (3D) nanostructure does not only provide fast electron transport, but also offers better ionic flux. Therefore, proper design of the nanostructured electrocatalysts is required to enhance the electrocatalytic activities and prolong the cycle life of the energy storage devices. [32, 38, 40-41]

Figure 2.3 (a) The mechanisms of electrolyzer and fuel cell on storage and conversion. (b) Schematic illustration of the thermodynamic potentials of OER/ORR: $\text{O}_2 + 4\text{e}^- + 4\text{H}^+ \leftrightarrow \text{H}_2\text{O}$ at 1.23 V *versus* NHE and thermodynamic potentials of HER/HOR: $4\text{e}^- + 4\text{H}^+ \leftrightarrow 2\text{H}_2$ at 0 V *versus* NHE. (c) To store energy, an electrolyzer is used to split water molecule into energy carriers (e.g. H₂ and O₂). (d) For energy conversion, a fuel cell is used to recombine O₂ and H₂ back to H₂O, while releasing energy for consumption.

In addition to Li-O₂ battery, the fuel cell is another high energy storage technology that involves electrocatalysis. The hydrogen fuel has been receiving a great deal of interest as it carries the greatest specific energy of 143 MJ kg⁻¹ in comparison with the rest of the energy storage devices. [42-43] To store energy, an

electrolyzer is utilized to convert H_2O molecules into energy carriers (*e.g.* O_2 and H_2). In the reverse process, a fuel cell is employed to convert fuel H_2 and O_2 back into H_2O molecules, while releasing energy for consumption (Figure 2.3a). The two half-cell equations of oxygen evolution reaction (OER)/oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER)/hydrogen oxidation reaction (HOR) have thermodynamic values at 1.23 V *versus* NHE and 0 V *versus* NHE, respectively (Figure 2.3b). The HER and OER reactions occur in the electrolyzer (Figure 2.3c), while the ORR and HOR processes occur in the fuel cell (Figure 2.3d). All the four reactions are equally important in the application of electrolyzer and fuel cell. In this thesis, we are focusing on the HER process.

Figure 2.4 (a) Voltage versus capacity profiles of Li-O₂ batteries with PtAu/C, Pt/C, Au/C at 100 mA g⁻¹, and C at 80 mA g⁻¹. (a) Reproduced with permission from [34]. Copyright © 2010. American Chemical Society. (b) Voltage versus capacity profiles of Li-O₂ batteries with Pt NPs@CNT at 250 mA g⁻¹. (b) Reproduced with permission from [44]. Copyright © 2014. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) Voltage versus capacity of Li-O₂ battery with Mo₂C/CNT at various current density. (c) Reproduced with permission from [45]. Copyright © 2015. American Chemical Society. (d) LSV curves of Mo-based material versus Pt/C for HER. (d) Reproduced with permission from [46]. Copyright © 2013. The Royal Society of Chemistry.

Presently, noble metal like Pt is a preeminent and the most efficient electrocatalyst in both the OER in Li-O₂ battery (*e.g.* Li-O₂ battery with Pt/C delivers ~ 3.6 V *versus* Li⁺/Li at 500 mA h g⁻¹)^[34] and HER (*e.g.* Pt/C electrocatalyst exhibits almost zero onset potential in acidic media),^[42] However, the expensiveness and the scarcity of Pt metal hamper its practical implementation.^[47] Unlike the high-priced Pt ($\sim \$100$ g⁻¹), the earth abundant and cheap non-noble metals, such as iron (Fe: $\sim \$0.0012$ g⁻¹), cobalt (Co: $\sim \$0.027$ g⁻¹), nickel (Ni: $\sim \$0.020$ g⁻¹), copper (Cu: $\sim \$0.011$ g⁻¹), molybdenum (Mo: $\sim \$0.00015$ g⁻¹) and tungsten (W: $\sim \$0.054$ g⁻¹), are more suitable for scalable production and realistic application.^[48] Among these non-noble metals, Mo-based material is considered to be a relatively cheaper material. Recently, studies have suggested that a novel category of Mo-based material (*e.g.* Mo₂C) electrocatalyst has emerged to possess similar electrocatalytic activity as compared to the Pt metal due to the similarity in their d-band electronic structure.^[46] Figure 2.4a and b demonstrate that the Li-O₂ battery with Pt/C has a charging voltage of more than 3.5 V *versus* Li⁺/Li at 100 mA g⁻¹ and 250 mA g⁻¹, respectively. Surprisingly, Li-O₂ battery with Mo₂C/CNT could achieve a charging voltage that is below 3.5 V *versus* Li⁺/Li even at a high current density of 250 mA g⁻¹ (Figure 2.4c). Additionally, Mo₂C/CNT exhibits low HER overpotential that is closer to the state-of-the-art Pt/C (Figure 2.4d). These advantages of Mo₂C material make it more promising to be an alternative Pt-free electrocatalyst for electrocatalysis related to OER and HER.

Figure 2.5 Heterogeneous redox reaction occurs at the electrode-electrolyte interface.

Electrocatalysis is a process that involves the use of electrocatalyst to expedite electrochemical reaction rate. Electrochemical reaction is redox reaction (*e.g.* reduction or oxidation) that comprises of the electron transfer on the electrode-electrolyte interface (Figure 2.5). Electrochemical reaction is also known to be heterogeneous reaction as the reactants are in different phases (*e.g.* electrons are in solid electrode phase, while the oxidant species are in liquid electrolyte phase). It is notable that there is no electron transfer occurring in the chemical reaction whereas there is a free electron transfer involves in the electrochemical reaction. In general, an electrochemical reaction can be written as: $\text{Ox}_{\text{species}} + n\text{e}^- \leftrightarrow \text{Re}_{\text{species}}$, where $\text{Ox}_{\text{species}}$ and $\text{Re}_{\text{species}}$ represent oxidized and reduced species, respectively. When this electrochemical reaction is at the equilibrium state, the equilibrium voltage (ΔE_{cell}) of the cell reaction is at its thermodynamic voltage, while the current (I) equals to zero ($I = 0$ is also known as the exchange current). After the voltage ($\Delta E_{\text{applied}}$) is applied across the electrodes, the electrochemical reaction is being driven forward, whereby $\Delta E_{\text{applied}} < \Delta E_{\text{cell}}$ and $I < 0$. On the contrary, the backward reaction has a $\Delta E_{\text{applied}} > \Delta E_{\text{cell}}$ and $I > 0$.

Figure 2.6 Schematic illustration of the ΔG_{rxn} and $\Delta G^{\ddagger}$ during reaction progress.

In a typical chemical reaction, the overall change in Gibbs free energy of reaction, ΔG_{rxn} , is the subtraction of Gibbs free energy between reactants and products, while the overall change in the Gibbs free energy of activation, $\Delta G^\ddagger$ is the difference of Gibbs free energy between reactant and transition state (Figure 2.6). The ΔG_{rxn} is defined by the GIBBS-HELMHOLTZ equation: ^[49]

$$\Delta G_{\text{rxn}} = \Delta H_{\text{rxn}} - T\Delta S_{\text{rxn}}$$

For the electrochemical cell reaction, the ΔG_{rxn} is the amount of theoretical input electric energy required to drive the electrochemical reaction, while the ΔH_{rxn} is the amount of output electric energy. The reversible reaction heat of the cell is defined by $T\Delta S_{\text{rxn}}$ term and it is also known as the PELTIER effect, ^[50] which tells us the reversible amount of heat consumed or released during the electrochemical reaction. At equilibrium state, the theoretical cell voltage (ΔE_{cell}) can be calculated using the relationships between ΔE_{cell} and ΔG_{rxn} : ^[51] $\Delta G_{\text{rxn}} = -z \times F \times \Delta E_{\text{cell}}$, where z symbolizes the number of electrons participated in one specific electrochemical reaction; F symbolizes the Faraday's constant; ΔE_{cell} represents the theoretical cell voltage, which is dependence on the concentration of reactant/product, temperature, and pressure.

As the reaction progress, the reaction rates are limited due to the impedance resistance (also known as activation energy barrier). Therefore, additional energy is required to overcome this activation energy barrier for any electrochemical reaction to proceed. At the peak of this barrier, a transition state is formed, which allow the reactant to undergoes the transition to the product. Lower the activation energy barrier makes the transition process easier to proceed.

According to Eyring-Polanyi equation, the reaction rate (in term of rate constant) is exponentially dependent on the degree of the activation energy barrier: ^[52] $k = Ae^{-(\Delta G^\ddagger/RT)}$, where k represents the rate constant; $A = k_B T/h$ (h represents the Planck's constant; T represents the absolute temperature; k_B represents the Boltzmann constant); $\Delta G^\ddagger$ symbolizes the change in the Gibbs free energy of activation; R represents gas constant.

To understand how does $\Delta G^\ddagger$ can be related to reaction rate and how rate of reaction can be associated with current flow in the electrochemical reaction, we need to do some derivations as shown below:^[53]

Rate of forward reaction: $v_{FW} = k_{FW} \times C_{O(0,t)} = Ae^{-(\Delta G^\ddagger_F/RT)} \times C_{O(0,t)} = i_c/zF$, where k_{FW} represents the rate constant of forward reaction; $C_{O(0,t)}$ represents the concentration of the oxidized species at time = 0 to finite number of time (t); $\Delta G^\ddagger_F$ represents the change in the Gibbs free energy of activation for forward reaction; I_c represents the cathodic current of forward reaction.

Rate of backward reaction: $v_{BW} = k_{BW} \times C_{R(0,t)} = Ae^{-(\Delta G^\ddagger_B/RT)} \times C_{R(0,t)} = i_a/zF$, where k_{BW} represents the rate constant of backward reaction; $C_{R(0,t)}$ represents the concentration of the reduced species at time = 0 to finite number of time (t); $\Delta G^\ddagger_B$ represents the change in the Gibbs free energy of activation for backward reaction; i_a represents the anodic current of backward reaction.

At the transition state, reaction either move forward or backward. To determine the net reaction rate: $v_n = v_F - v_B = A(e^{-(\Delta G^\ddagger_F/RT)} \times C_{O(0,t)} - e^{-(\Delta G^\ddagger_B/RT)} \times C_{R(0,t)}) = (i_c - i_a)/zF$

At open circuit voltage, the system is at equilibrium state, $v_F = v_B$ and $i_c = i_a = i_o$ where i_o is the exchange current. At this equilibrium state, the equilibrium cell voltage is defined as ΔE_{cell} .

When an applied voltage ($\Delta E_{applied}$) is supplied to move the electrochemical reaction away from the equilibrium, and the currents flow causes a shift in the voltage of the equilibrium cell reaction, which also influences the activation barrier. The deviation of voltage from equilibrium cell reaction is called overpotential, η . And the $\Delta E_{applied}$ is defined in the following equation:^[53] $\Delta E_{applied} = \Delta E_{cell} + \sum |\eta|$, where $\sum |\eta| = |\eta_{CT}| + |\eta_D| + |\eta_o|$

It is obvious that the sum of overpotentials must be minimized. The overpotentials have different origin:^[53]

- (1) Charge transfer overpotential, η_{CT} : the overpotential required to transfer charges at the electrode-electrolyte interface is defined as the charge

transfer overpotential. Formulae that deal with this η_{CT} are the Butler-Volmer equation and the Tafel equation

The Butler-Volmer equation denotes the relationship between current, surface concentration and charge transfer overpotential (also known as activation voltage loss during electrochemical processes) at a net current: $i = i_o (C_{O(0,t)}/C_O^* e^{-\alpha n F \eta / RT} - C_{R(0,t)}/C_R^* e^{(1-\alpha) n F \eta / RT})$ where, $C_{O/R}^*$ represents the bulk concentration and α represents the transfer coefficient.

When there is no mass transfer, $C_{O(0,t)}/C_O^*$ and $C_{R(0,t)}/C_R^*$ are approximately equal to 0.9 to 1.1.

Butler-Volmer behaviour for $|\eta|$ is small, the exponential e^x can be approximated as $1 + x$, therefore $i = i_o \times n F \eta / RT$; $\eta / i = RT / n F i_o = R_{CT}$ where R_{CT} is the charge transfer resistance.

Tafel behaviour for $|\eta|$ is large, $e^{-\alpha n F \eta / RT} \gg e^{(1-\alpha) n F \eta / RT}$, therefore $i = i_o \times e^{-\alpha n F \eta / RT}$; $\eta = RT / \alpha n F \times \ln i_o - RT / \alpha n F \times \ln i$; $\eta = a \times \ln i + b$ where $a = -RT / \alpha n F$ and $b = RT / \alpha n F \times \ln i_o$

Plot η versus $\ln i$ to find Tafel slope = a and the y-intercept = b .

- (2) Diffusion overpotential, η_D : The depletion of reacting species near the electrode surface, leading to the concentration polarization. The reaction kinetics is established by the diffusion processes through Nernst layer.
- (3) Ohmic overpotential, η_o : Ohmic polarization caused by the internal resistance of the electrolyte, electrodes, etc)

Figure 2.7 Cell overpotentials as a function of operating current.

The change in the voltage of the electrochemical cell reaction is summarized in Figure 2.7. The overall cell voltage is shifted away from equilibrium cell voltage. The voltage that losses due to ohmic overpotential is lost as joulic heat $W_J = I^2 \times \eta_o \times t$, while the voltages loss due to charge transfer overpotential and diffusion overpotential are lost as thermal heat $W_k = I \times (|\eta_{CT}| + |\eta_D|) \times t$.

2.1.1 Literature review on the wetting property of the TMBE for electrocatalysis

The interaction of metal oxide (MO) with adsorbate (*e.g.* O₂ and H₂O) plays a crucial role in the applications, such as electrocatalysis,^[54] and wetting.^[55] The MO-adsorbate interface is one of the key components in electrocatalysis.^[56] The unique ionic-covalent characteristics^[57] of the MO has a significant influence on the absorptivity between MO and adsorbates,^[58] wetting properties,^[55] and electrocatalytic activities.^[59] Here we review the “wetting” property of MO surfaces and relates it to the electrocatalysis involving with oxygen activity.

Conventional contact angle (CA) measurements provide information on the wettability between water and the MO. This wettability is depending on the interfacial energy of the adsorbate/ MO interface. The reduction of the interfacial energy, resulting in the decrement of CA, and thus improves the wettability between the adsorbate (*e.g.* H₂O or Li₂O₂) and MO. The interaction between water and MO depends greatly on the electronic structure of the adsorbate-MO hybrid. In general, the MO that possesses a higher degree of polarity also exhibits a higher degree of hydrophilicity. Recently, Sun et al. has demonstrated that different architectures of the catalyst could also influence the interaction between the gas molecules and the catalyst surface, such as, the gas molecules exhibit less adhesion on the MoS₂ nanostructured film as compared to MoS₂ flat film.^[60, 61]

Figure 2.8 (a) In general, MOs are hydrophilic as their electronic structure favors the formation of H-bond with H_2O molecules. For example, the oxide at the surface of the Al_2O_3 forms H-bond with the H atom on the H_2O molecule, while the empty (3p) orbital of Al atom at the surface of Al_2O_3 is electron deficient and it interacts with the O atom on the H_2O molecule. These strong interactions lead to a contact angle of $<10^\circ$ being obtained, indicating that the Al_2O_3 is hydrophilic in nature. (b) On the other hand, the empty orbital on (4f) inner shell of R^{3+} on the surface of the R_2O_3 are shielded by the octet outer 5s and 5p orbitals, which hidden the interaction between the O atom on H_2O and R^{3+} . As a result, a contact angle of $\sim 102^\circ$ is obtained, representing that the R_2O_3 is hydrophobic in nature. (a-b) Reproduced with permission from ^[55]. Copyright © 2013. Nature Publishing Group.

With high or complete polarity (characteristic close to ionic), MO could facilitate the orientation of the H_2O molecules to form hydrophilic hydration structure.^[62-63] For instance, Al_2O_3 possesses high polarity characteristic, owing electron-deficient Al atom and electron-rich O atoms that serve as Lewis acid and Lewis base, respectively.^[64] The unsaturated sites on the three sp^2 orbitals of Al atom at the surface of Al_2O_3 allow the lone pair on the O atoms of H_2O to form dative covalent bond, resulting in the formation of hydrophilic hydration structure,^[65-66] showing an excellent wetting property with a contact angle of $\sim 10^\circ$ (Figure 2.8a).^[55] On the contrary, the empty 4f orbitals of metals (R^{3+}) on the surface of

the rare-earth oxide (R_2O_3) are shielded by the octet $5s^2p^6$ outer shell.^[67-68] As a result, the R^{3+} metals have a lower tendency to form a dative-covalent bond with the O atom on the H_2O molecule. Hence, the orientation of the H_2O molecules on the surface of the R_2O_3 arranges in such a direction that the O atom of the H_2O points away from the R_2O_3 surface caused by electron-electron repulsion, meanwhile this O atom (on H_2O) forms hydrogen bonding (H-bonding) with the neighboring H_2O molecules, leading to the formation of hydrophobic hydration structure with a high CA of $\sim 102^\circ$,^[55] as illustrated in Figure 2.8b. Although materials, such as R_2O_3 are hydrophobic in nature, it's hydrophilicity can be altered by polymeric surface modification.^[69] However, as mentioned earlier in section 2.1, the formation of reactive O_2^{2-} during discharging of Li- O_2 battery tends to decompose the organic polymers (*e.g.* polyethylene glycol and polypropylene).^[70-71] Therefore, the usage of the organic polymer to modified the metal oxide's hydrophilicity is not desirable.

Figure 2.9 Contact angles (θ) measured experimentally as a function of the logarithm of the molar fraction of oxygen dissolved ($\log X_O$) in the MO. Reproduced with permission from ^[72]. Copyright © 2001. Elsevier Science.

Typically, the word “wetting” defines the interaction that involves H_2O molecule as the adsorbate, but sometimes it can also mean that the adsorbate (*e.g.* adsorbate

can be solid, liquid or gaseous) can form a uniform layer on top of the substrate. There are several common terms that define “wetting” such as: (1) low interfacial energy; ^[73] (2) small lattice mismatch; ^[74] (3) large number of chemical interactions formed at the adsorbate-substrate interface; ^[75] (4) strong affinity/strong interaction between the adsorbate and the substrate. ^[76]

In 1993, Fouletier *et al.* have established a correlation between the wettability and O₂ activity on a MO-gold system. He built a machine consists of a sessile drop in combine with an O₂ sensor to measure the wetting property and partial pressure of oxygen (Po₂), respectively.^[77] In addition, he found out that the copper oxide/gold material exhibits better wetting property and higher O₂ activity (lower Po₂ is being measured as a higher number of O₂ molecules is being adsorbed on the surface of the material) of as compared to pure gold.^[78] However, this relationship between the wettability and O₂ activity is still unclear. Until in the year of 2001, Muolo *et al.* have demonstrated an exponential relationship between the contact angle (θ) and O₂ activity. The θ in y-axis represents wetting property between H₂O adsorbate and substrate and the molar fraction of dissolved oxygen (X_o) in x-axis represents the O₂ activity (Figure 2.9).^[72] The θ decreases exponentially with the increase in X_o, implying that as the wetting property of the materials enhances, the O₂ activity also improves.

Figure 2.10 Schematics illustration of the nucleation and growth pathways of newly formed ZnO adsorbate (represented by green color) on the existing Au-ZnO substrate

(ZnO represents as blue color) and Au represents as red color) at a condition when the interfacial energy of adsorbate-substrate is (a) high or (b) low. γ_{33} represents the surface energy of existing ZnO and newly formed ZnO via path A and γ_{13} represents the surface energy of existing Au and newly formed ZnO via path B. (a-b) Reproduced with permission from [79]. Copyright © 2013. American Chemical Society.

Moreover, the morphology of adsorbate deposited on the existing substrate is also depending on the interfacial energy between the adsorbate-substrate interface. For example, the growth of the newly formed ZnO adsorbate favors path A as it has a lower interfacial energy on existing ZnO ($\gamma_{33} < \gamma_{13}$) in comparison with existing Au (via path B), resulting in localized nucleation of the ZnO adsorbate on the ZnO substrate but not on the Au substrate, forming a spherical ZnO on the Au, as shown in Figure 2.10a. On the other hand, if the formation of ZnO adsorbate favors both path A and B as they have similar adsorbate-substrate interfacial energy, the substrate will exhibit multiple nucleation sites for ZnO adsorbate to deposit uniformly on it, forming core-shell Au-ZnO structure (Figure 2.10b).

2.1.2 Literature review on the nanostructured porous TMBE for electrocatalysis.

Figure 2.11 N₂ adsorption/desorption isotherms measurement with inset pore size distribution of a porous sample. Reproduced with permission from [80]. Copyright © 2013. The Royal Society of Chemistry.

Porous materials are advantageous and propitious to be utilized for electrocatalysis, gas storage, batteries and capacitive energy storage.^[81-85] The pore size distribution (PSD) and the specific surface area (SSA) of porous materials are frequently characterized by nitrogen adsorption/desorption isotherms using Micromeritics ASAP 2020 analyser, as shown in Figure 2.11. Porous materials are commonly classified into three categories: (1) micropores (pore size < 2 nm); (2) mesopores (pore size between 2–50 nm); (3) macropores (pore size > 50 nm). Smaller pore size has smaller ion-transport resistance (higher ion diffusivity).^[83] Most importantly, such porous materials increase the SSA, leading to high electrocatalytic activities.

Figure 2.12 (a) XRD spectrums of the $\text{Mn}_{0.1}\text{Ni}_1$ electrodes calcined at 300 °C under various annealing durations (*e.g.* 0, 3, 19, and 15 h) and their corresponding (b) polarization curves of OER. (c) The SSA of the electrodes and OER current densities along the y-axis are plotted against different annealing periods (oxidation time). (a-c) Reproduced with permission from^[86]. Copyright © 2015. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Shalom *et al.* have demonstrated that through the annealing process of $\text{Mn}_{0.1}\text{Ni}_1$ electrocatalysts at 300 °C under various annealing durations (0, 3, 10 and 15 h), the sample's SSA could be modified. According to the writer, the morphology of the $\text{Mn}_{0.1}\text{Ni}_1$ electrode does not have significant change when annealing periods are 0, 3, and 10 h. However, the crystalline size increase from ~5 nm (at 10 h annealing time) to ~15 nm (at 15 h annealing time) and the values of the X-ray diffraction (XRD) peaks using the Scherrer equation (Figure 2.12a) are employed as the basis for the calculations. Figure 2.12b displays the OER polarization curves of the $\text{Mn}_{0.1}\text{Ni}_1$ electrodes at different annealing periods, and Figure 2.12c

exhibits that the OER activity can be enhanced as the SSA of the electrocatalyst increases. It is being proposed that larger SSA provides more catalytic sites for OER, and thus improves the electrocatalytic activity.

Figure 2.13 (a) Schematic synthesis of mesoporous MoS₂ with a DG morphology. (b) HRTEM image of the DG-MoS₂ consists of a pore size estimated to be 7 nm and [311] and [211] planes are being observed. (c) HER measurements of DG-MoS₂ in comparison with core-shell MoO₃-MoS₂ nanowires. (a-c) Reproduced with permission from [87] Copyright © 2012. Nature Publishing Group.

The fabrication of porous material assists the mass transportation of protons from the bulk electrolyte to the electrode surface and it is essential for HER. Moreover, different pore sizes have a different effect on the ion diffusivity. For instance, double-gyroid (DG) structure (pore size ~7 nm) displays a diffusivity higher than other mesoporous structure (pore size 2–50 nm).^[88] Jaramillo *et al.* have fabricated 3D mesoporous MoS₂ network structure, as presented in Figure 2.13a. The high-resolution transmission electron microscopy (HRTEM) image (Figure 2.13b) exhibits that the as-synthesized MoS₂ with a DG morphology obtains a

pore size of about 7 nm. The HER activity of the DG-MoS₂ shows an obvious lower operating potential at 10 mA cm⁻² in comparison with the existing core-shell MoO₃-MoS₂ nanowires (Figure 2.13c). These results indicate that 3D DG-MoS₂ has better HER activity than 1D MoO₃-MoS₂. The superior HER performance of the DG-MoS₂ material is attributed to several structural advantages: (1) 3D structure is interconnected, which facilitates fast ion and electron transportation; (2) porous structure possesses large SSA could provide a more active sites for HER.

Figure 2.14 (a) Synthetic approach for fabricating porous MoSe NSs. (b) Low-magnification TEM image of the porous MoSe₂ NSs. (c) LSV profiles consist of commercial Pt/C catalysts, nonporous MoSe₂ NSs and the porous MoSe₂ NSs. (a-c) Reproduced with permission from ^[89] Copyright © 2016. The Royal Society of Chemistry.

Recently, Wu *et al.* have synthesized porous MoSe₂ via oxidant-assisted exfoliation (Figure 2.14a). The TEM image (Figure 2.14b) shows that the as-prepared MoSe₂ materials are highly porous. The HER measurements show that the porous MoSe₂ nanosheets have a smaller onset potential of 75 mV in comparison with the nonporous MoSe₂ (onset potential of 220 mV), as presented in Figure 2.14c. These results further prove that porous material indeed has much superior HER activity over the nonporous material.

Figure 2.15 (a) Schematic illustration on the synthetic routes for making MoO₂ on PC and RGO. (b) HRTEM images of the MoO₂@PC-RGO sample. (c) LSV curves of MoO₂@PC versus MoO₂@PC-RGO in 0.5M H₂SO₄ solution. (a-c) Reproduced with permission from ^[90] Copyright © 2015. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Recently, metal-organic frameworks (MOFs) and Mo-based polyoxometalate (POM) have attracted much interest for electrocatalysis as they are highly porous.^[91-92] The porous structure of MOFs and POMs offers a unique structural advantage for synthesizing metal oxide-carbon hybrid material. Yu *et al.* have fabricated a MoO₂ on porous carbon/reduced graphene oxide (MoO₂@PC-RGO) electrocatalysts via the POMOF/GO-assisted strategy, as presented in Figure 2.15a. Initially, the Mo-based POM was encapsulated in the carbon-based MOFs supported on GO. Then the resultant product undergoes annealing to form MoO₂ particles supported on PC-RGO template (Figure 2.15b). The porous MoO₂@PC-RGO electrode possesses an electrochemical surface area (ECSA) of 131.2 mF cm⁻².^[90] This porous structure exhibits low operating potentials and excellent electrochemical/structural stability in acidic medium (Figure 2.15c).

2.1.3 Literature review on the electronic structure of metal-adsorbate for HER

Table 2.1 Summary of the various type of HER pathways in acidic and alkaline media respectively.

Overall cell reaction	Various reaction pathways
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ (Acidic media)	$\text{H}^+ + \text{e}^- + * \rightarrow \text{H}^*$ (Volmer) $\text{H}^+ + \text{e}^- + \text{H}^* \rightarrow \text{H}_2$ (Heyrovsky) or $2\text{H}^* \rightarrow \text{H}_2$ (Tafel)
$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (Alkaline media)	$\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}^* + \text{OH}^-$ (Volmer) $\text{H}_2\text{O} + \text{e}^- + \text{H}^* \rightarrow \text{H}_2 + \text{OH}^-$ (Heyrovsky) or $2\text{H}^* \rightarrow \text{H}_2$ (Tafel)

The detailed mechanisms of HER in acidic and alkaline media are summarized in Table 2.1.^[93] Volmer reaction is known to be the first step for HER. For Volmer reaction in the acidic media, the electron is being transferred from the electrocatalyst's surface to the H^+ , forming catalyst-H (named as H^*). In contrast, HER in the alkaline requires an additional energy barrier to overcome the dissociation of water molecules, and thus this may affect the reaction rate. In the subsequent step, the HER undergoes either the Heyrovsky or Tafel reaction pathway. For the Heyrovsky reaction, the H^* combines with the electron from the electrocatalyst, forming H_2 molecule. For Tafel reaction, the two adjacent H^* combine together to form one H_2 molecule. The reaction pathways can be determined using a Tafel slope. The Tafel slopes of 120, 40, 30 mV dec^{-1} are prediction guidelines for HER undergoing Volmer, Heyrovsky, and Tafel reaction pathways, respectively.^[94]

Figure 2.16 Proposed mechanisms for hydrogen evolution reaction via homolytic or heterolytic pathways. M represents the metallic electrocatalysts. Reproduced with permission from ^[95] Copyright © 2013. The Royal Society of Chemistry.

Chang *et al.* have proposed that the catalytic cycle for hydrogen production undergoes either homolytic or heterolytic pathways, as illustrated in Figure 2.16. The HER proceeds with a starting material, metal hydride intermediate ($H-M^{n+1}$). Creutz *et al.* have proposed that this metal hydride is formed through the oxidative addition of H_3O^+ on metal complex. ^[96] Homolytic reaction is quite similar to the Tafel reaction in Table 2.1. In a homolytic reaction, two $H-M^{n+1}$ complexes combine together to release H_2 molecule via reductive elimination. While, the heterolytic reaction is similar to Heyrovsky reaction in Table 2.1. In the heterolytic reaction, $H-M^{n+1}$ complex is being reduced by electron followed by reacting with H^+ ion to form H_2 molecule.

Figure 2.17 (a) ΔG_{H^*} versus the reaction coordinate. (b) ΔG_{H^*} diagram of various electrocatalysts (e.g. N-graphene, Pt, $C_3N_4@NG$, and g- $C_3N_4@NG$) for HER. (b) Reproduced with permission from [97]. Copyright © 2014. Nature Publishing Group. (c) The relationship between the logarithm of exchange current density ($\log i_0$) versus ΔG_{H^*} . (c) Reproduced with permission from [98] Copyright © 1958. Royal Society of Chemistry. (d) i_0 versus ΔG_{H^*} of various monometallic, non-metallic and composite materials. (d) Reproduced with permission from [97]. Copyright © 2014. Nature Publishing Group.

Figure 2.17a shows the Gibbs free energy change of hydrogen adsorption (ΔG_{H^*}) diagram for HER. The ΔG_{H^*} is plotted along y-axis against the HER reaction coordinate. If the ΔG_{H^*} value is negative, it implies that the metal-adsorbate interaction is strong. Whereas, if the ΔG_{H^*} value is positive, it indicates that the metal-adsorbate interaction is weak. In an ideal case, the free energy state of reaction intermediate should be the same as the energy states of both the reactant and product. According to Sabatier principle, [99] an ideal catalyst is defined as the binding strength of the reaction intermediate should neither be strong nor weak. If the interaction is too strong, the active site of the catalyst will be poison.

Whereas, if the interaction is too weak, no reaction will occur. Therefore, a good catalyst should have an optimum binding energy where the ΔG_{H^*} value is equal or close to zero. The use of different electrocatalysts will result in different H adsorption free energy due to different metal-adsorbate binding energy. For instance, this binding energy (indication by ΔG_{H^*}) can be calculated using density functional theory (DFT), as shown in Figure 2.17b. Pt electrocatalysts is well-known to be state-of-the-art for HER as it exhibits excellent HER activity and it is supported by the free energy diagram. Since Pt metal has a ΔG_{H^*} value that is near to zero in comparison with the other electrocatalysts, it indicates that the former is a better HER electrocatalyst.

By plotting i_0 against $\Delta G(U_0)$, a volcano plot is obtained (Figure 2.17c). This volcano plots play an important role for electrocatalysis as it acts as a benchmark of the newly synthesized electrocatalyst in comparison with other existing electrocatalysts, whereby the point (determined by i_0 and ΔG_{H^*} values) located nearer to the peak of the volcano-shaped plot, representing a good catalyst with a better electrocatalytic activity. For example, Qiao *et al.* have demonstrated the use of volcano plot (Figure 2.17d) to benchmark his sample: $C_3N_4@NG$ (marked by red triangle) and it is being stated that the HER activity of this sample is comparable with that of the existing MoS_2 sample.

Figure 2.18 (a) The mixing of adsorbate and the metal energy levels. (a) Reproduced with permission from ^[100]. Copyright © 2005. Springer Link. (b) Schematic representation of the interaction between adsorbate orbital and metal d band orbital, forming a bonding metal-adsorbate states (with a new d band) and an anti-bonding metal-adsorbate states. (b) Reproduced with permission from ^[101]. Copyright © 2010. The Royal Society of Chemistry. (c) Top: Experimental measurements of the occupied states and unoccupied states of N adsorbed on the Ni(100) and Cu(100) surface using XES and XAS, respectively. Bottom: Theoretical calculation of density of states of P_{xy} and P_z valence states of N adsorbed on Ni(100) and Cu(100) surface. Black line represents the occupied energy level (on the left side of Fermi level), while the gray line represents the unoccupied energy level (on the right side of Fermi level). (c) Reproduced with permission from ^[100]. Copyright © 2005. Springer Link. (d) Energy (ϵ) versus DOS of adsorbed H atom on the Ni(111), Cu(111), Pt(111) and Au(111) surface with arrows pointed at the anti-bonding of H 1s–d metal state. Unoccupied energy levels are represented in white and occupied energy levels are represented in gray. (d) Reproduced with permission from ^[102]. Copyright © 1995. Nature Publishing Group.

The d-band model (Figure 2.18a) is a molecular orbital model, which is used to illustrate the interaction of the adsorbate and metal catalyst. When the metal d-band orbital and the adsorbate orbital are mixed, a new bonding metal-adsorbate states (consists of newly formed d-band) and a new anti-bonding metal-adsorbate states are formed, as illustrated in Figure 2.18b. These bonding and anti-bonding energy states could be measured by utilizing the X-ray emission spectroscopy (XES) and the X-ray absorption spectroscopy (XAS) respectively (Figure 2.18c). Reducing the d-band center (has a lower the anti-bonding state) will weaken the hydrogen adsorption strength, whereas higher d-band states with respect to Fermi level will result in higher anti-bonding state (has a stronger metal-adsorbate bond). When the d-band centers are lower than the Fermi level (as denoted by the black arrow for the Au(111) and Cu(111) surfaces in Figure 2.18d), the probability of filling the anti-bonding orbital increases and the metal-H bond becomes destabilized. On the contrary, if the d-band centers for Ni(111) and Pt(111) surfaces are above the Fermi level (as denoted by the black arrow in

Figure 2.18d), the chances of filling electrons into these anti-bonding states will be low, which also indicates that a higher d-band center will induce a stronger metal-adsorbate bond.

Figure 2.19 ΔG_{H^*} versus $E_d - E_F$. All the values of ΔG_{H^*} are taken from reference ^[103] and the values for $E_d - E_F$ are taken from reference ^[104].

A linear relationship between ΔG_{H^*} and the d-band center with respect to Fermi level, $E_d - E_F$ is illustrated in Figure 2.19. It implies that metal with a higher d-band center (i.e. a lower $|E_d - E_F|$ value) has a more negative ΔG_{H^*} . This theoretical prediction indicates that the metal-adsorbate bond is strong. From this plot, we can observe that Pt exhibits an optimum ΔG_{H^*} values (close to zero), which has a $|E_d - E_F|$ value close to ~ 2.25 (near to Fermi level). This theoretical evaluation matches with the experimental result based on the volcano plot in Figure 2.5.2 d. For example, the Pt electrocatalyst (with ΔG_{H^*} value close to zero) has the highest i_o (high i_o value indicates better HER activity).

Figure 2.20 Molecular orbital bonding of σ donation (*e.g.* $M \leftarrow H_2$) and π back donation (*e.g.* $M \rightarrow H_2$). Reproduced with permission from ^[105]. Copyright © 2009. The Royal Society of Chemistry.

In the field of organometallic chemistry, electron density in the metal center determines the fate of bond formation or bond breaking. For example, if the metal center is electron deficient, the adsorbate ligand will form bond with the metal center via the σ -donation. On the other hand, if the metal center is electron rich, it facilitates the π -back donation of the electron from the metal d-orbital to the antibonding orbital of the adsorbate, leading to bond breakage of the adsorbate (Figure 2.20).^[105]

2.2 Question to answer and PhD in context based on literature in section 2.1.1

Question: How does the wetting property of MO lower the charging voltage of Li-O₂ battery?

Answer: During discharging of the Li-O₂ battery, Li₂O₂ form on the surface of electrocatalysts via the following mechanism: $2Li^+ + 2e^- + O_2 \rightarrow Li_2O_2$. The morphology of Li₂O₂ forms during discharging depends on the “wetting” ability between Li₂O₂ and MO on the electrocatalysts surface. Based on the literature, there are several possible hypotheses for this “wetting” phenomenon: (1) transition MO possesses an ionic characteristic that exhibits good wetting property toward H₂O molecules (MO interacts with H₂O via hydrogen bonding, forming hydration structure). In this context, we propose that this unique intrinsic property might provide good ionic interaction between metal oxide (*e.g.* IrO₂ or CuO) based electrode and Li₂O₂ product, forming Li₂O₂ thin layer on electrocatalysts’ surface; (2) MOs tend to have better affinity towards O₂ as compare to noble metal; (3) lower interfacial energy between the adsorbate (*e.g.* Li₂O₂) and the substrate (*e.g.* MO-based electrocatalyst); the existence of

multiple nucleation sites on the substrate (*e.g.* CuO NPs acts as nucleation sites on the Pt substrate) could facilitate the formation of core-shell structure (*e.g.* CuO/Pt is the core, while Li_2O_2 thin layer is the shell). Therefore, by introducing metal oxide on the electrocatalysts' surface, we could improve the "wetting" affinity towards Li_2O_2 , forming Li_2O_2 thin layer, which provides a short electron pathway for OER, resulting in lowering of charging voltage.

PhD in context: To test out the above "wetting" hypothesis, we have fabricated two different MOs on Pt catalysts' surface (*e.g.* CuO/Pt and IrO_2/Pt), and Pt (Pt acting as a control experiment) oxygen electrodes. During discharging of the Li- O_2 battery, we observe that electrodes' surface containing MOs (*e.g.* CuO/Pt and IrO_2/Pt) contain Li_2O_2 thin layers, while pure Pt electrode contains large spherical Li_2O_2 NPs. The structure of the Li_2O_2 are being observed under the TEM measurements and the presence of Li_2O_2 is being characterized using X-ray Photoelectron Spectroscopy (XPS). This Li_2O_2 thin layer in the MO-based battery exhibits a lower charging voltage as compared to large spherical Li_2O_2 in the Pt battery. It is being proposed that this Li_2O_2 thin layer provides a short electron pathway for OER, resulting in lowering of charging voltage.

2.3 Question to answer and PhD in context based on literature in section 2.1.2

Question: How does the TMBE with different pore sizes affect the electrocatalytic activities?

Answer: Based on the literatures, TMBE with porous structure exhibits superior electrocatalytic activities and the reasons are as such: (1) porous material tends to have a high SSA, which contributes more active sites for reaction to take place, resulting in a better reaction kinetics; (2) high SSA materials tends to have high surface defects, such as, oxygen and metal vacancies, which give a great effect on the electronic structure of materials, resulting in the lowering of resistance;

^[106] (3) smaller pore size has a smaller ion-transport resistance, which enhances the mass transportation rate of the reacting species to the surface active sites of the electrocatalyst. The prospective of this nanostructured Mo₂C could be used for water adsorption application. ^[107]

PhD in context: In this thesis, we have replaced the state-of-the-art Pt with an alternative Pt-free electrocatalyst (*e.g.* Mo₂C) for HER. The advantages of using Mo₂C over Pt as HER electrocatalysts are mentioned earlier in section 2.1. To evaluate the effect of different pore sizes TMBEs for HER, we have fabricated microporous Mo₂C and mesoporous Mo₂C for HER. Our HER measurements show that microporous Mo₂C has a lower HER operating potential as compared to mesoporous Mo₂C. This low HER operating potential of microporous Mo₂C is attributed to a bigger SSA and a shorter ion transport pathway.

2.4 Question to answer and PhD in context based on literature in section 2.1.3

Question: How can we tune the electronic structures of the TMBE to improve the electrocatalytic activities?

Answer: According to Sabatier principle a good catalyst neither binds to the adsorbate strongly nor weakly. To be an ideal catalyst: (1) the metal center must have the ability to donate and accept the electron, which facilitates a moderate metal-adsorbate interaction; (2) the theoretical ΔG_{H^*} value of the metal-adsorbate intermediate must be close to zero for HER (ΔG_{H^*} value is derived from DFT calculation). HER electrocatalysts with optimum ΔG_{H^*} value (ΔG_{H^*} close to zero) exhibits higher HER activity (indicated by higher exchange current density, i_0) as compared to electrocatalysts with ΔG_{H^*} value that deviates far away from zero.

PhD in context: In this research, Mo₂C-based material is chosen as a HER electrocatalyst due to its intrinsic properties as mentioned in section 2.1. To

investigate the electronic properties of the Mo_2C in HER, we have fabricated nitrogen-sulfur (N/S) co-doped Mo_2C in comparison with singly doped Mo_2C (*e.g.* N-doped Mo_2C and S-doped Mo_2C), and pure Mo_2C electrocatalysts. The HER performances of these electrocatalysts were evaluated and from our HER results, the N/S-doped Mo_2C exhibits the best HER activity. We believe that this excellent HER performance could be attributed to the dual properties of N (electron acceptor) and S (electron donor) in N/S-doped Mo_2C sample, which could provide synergistic effect for moderate metal-adsorbate interaction, and thus improved the HER activity. In addition, we have performed DFT calculation to verify the experimental HER trends: $\text{Mo}_2\text{C} < \text{N-doped Mo}_2\text{C} < \text{S-doped Mo}_2\text{C} < \text{N/S-doped Mo}_2\text{C}$. And it seems like our DFT results are in accordance with the experimental results.

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Chapter 3

Experimental Methodology

The rationale for the selection of materials/synthesis methods/characterization methods will be discussed in this chapter. Next, the working principles of the synthesis methods will be elaborated. Lastly, the working principles, analyses, and limitations of each characterization techniques will be presented.

3.1 Rationale for the selection of materials and methods

3.1.1 Selection of materials

The rationale for the material selection in various Chapters are listed below:

The major challenge for Li-O₂ battery is the high charging voltage caused by sluggish oxygen evolution reaction (OER) kinetics. This high charging voltage that exceeded 4.0 V *versus* Li/Li⁺ will lead to the degradation of the carbon-based cathode.^[1] Therefore, rational-design of the electrocatalysts with the aim of lowering the charging voltage will be discussed in Chapter 4. In Chapter 4, we will also discuss on the “wetting” affinity of metal oxides (MOs), such as IrO₂ or CuO supported on Pt towards Li₂O₂, forming Li₂O₂ thin layers during the discharging of the Li-O₂ battery. This Li₂O₂ thin layer provides a shorter electron transport pathway, therefore enhances the OER kinetics and lowers the charging voltage of Li-O₂ battery. As discussed earlier in section 2.1.1 and 2.2, MO is preferably selected over noble metal for Li-O₂ battery due to the intrinsic properties of MO (*e.g.* ionic characteristic of MO and the strong affinity of MO towards oxygen molecules). These aforementioned properties promote the formation of Li₂O₂ thin layer, which are important for achieving a low charging voltage. Initially, we choose Pt as an OER catalysts over other noble metals (*e.g.* Au), because Pt exhibits a better OER activity.^[2] Until recently, Liao *et al.* have demonstrated that IrO₂ catalyst has an equal or even higher OER activity than Pt.^[3] Based on these research findings, we have fabricated IrO₂ on conducting Pt to lower the charging voltage even further. However, Ir-based materials are rare and costly, which is not desirable for practical applications. Therefore, we replaced the IrO₂ with a cheaper MO material (*e.g.* CuO). Apart from IrO₂, Pt metal is equally scarce and expensive, therefore we replaced the Pt electrocatalysts with a low-cost and abundant Mo₂C material for further studies on other electrocatalytic processes (*e.g.* HER). As mentioned earlier in section 2.1, the Mo₂C material has similar electronic band structure to that of Pt, which makes it promising to replace Pt for HER.^[4-5] In addition, carbides materials usually exhibit excellent electrical conductivity and superior corrosion tolerance, which

allow them to withstand harsh pH conditions.^[6] Motivated by these advantages of Mo₂C material, we have synthesized Mo₂C-based electrocatalysts for HER in the subsequent two chapters. In Chapter 5, we have fabricated microporous Mo₂C versus mesoporous Mo₂C to evaluate the effect of different pore sizes electrocatalysts for HER. In Chapter 6, we have synthesized N/S co-doped Mo₂C in comparison with singly doped Mo₂C (*e.g.* S-doped Mo₂C and N-doped Mo₂C), and pure Mo₂C electrocatalysts to investigate the electronic properties of chemically doped Mo₂C towards HER.

3.1.2 Selection of synthesis methods

Chapter 4 presents the preliminary testing for “wetting” behavior between the MO and Li₂O₂ in Li-O₂ battery. We have synthesized the CuO nanoparticles (NPs) on the Pt nanowires (NWs) and the IrO₂ NPs/Pt NWs via a 3-step synthetic approach. In the first step, Pt NWs are fabricated via solvothermal reaction. In the subsequent step, metal hydroxide is deposited on the Pt NWs surface through precipitation process in alkaline solution. In the last step, metal hydroxide on Pt NWs is converted to MO through hydrothermal treatment. This synthetic approach is facile and it enables us to produce a large scale of MO/Pt materials for numerous Li-O₂ batteries testing. However, these NWs structure does not create a good electrical contact with the current collector, resulting in a limited rate capability and restricted capacity induced by the ohmic polarization. To resolve this issue, we grew Pt nanosheets (NSs) directly on the current collector, such as stainless steel mesh (SSM) via thermal decomposition followed by electrodeposition of CuO NPs uniformly on the Pt NSs substrate. This newly designed three-dimensional (3D) structural does not only provide good electrical contact, but also hastens the reactant’s diffusion rate from the electrolyte to the cathode surface, further enhances ORR kinetics and thus allows the Li-O₂ battery to achieve high specific capacity even when it is operating at a high current density.

As discussed in the previous section, we have replaced the expensive Pt with a

cheaper and plentiful Mo_2C for HER. There are several ways we can synthesize metal carbides material: (1) fabricating the carbon template first via solvothermal/hydrothermal treatment, then precipitating the metal precursor on carbon template followed by carburization (presented in Chapter 5); (2) synthesizing the metal/carbon hybrid through hydrothermal treatment the mixture containing carbon and metal precursors followed by carburization (discussed in Chapter 6); (3) synthesizing the MO first through hydrothermal reaction, then coating a layer of carbon precursor on the MO before carburization takes place (elaborated in Chapter 7).

In general, the metal carbide material can be easily obtained via hydrothermal/solvothermal treatment followed by carburization under H_2/Ar atmosphere. This approach is a simple method to produce a scalable product, which can be utilized for further characterizations and HER testing. Another method such as solvent exfoliation has also been incorporated in Chapter 6 to separate the layered sheet Mo_2C into single layered nanosheets. The exfoliation of layered Mo_2C into single sheets could improve the SSA, providing large active sites for HER. Solvent exfoliation method is chosen due to its high yield and high purity of single nanosheets in comparison with other exfoliation methods (*e.g.* Li-intercalation method), as discussed in section 3.2.5.

3.1.3 Selection of characterization techniques

These as-prepared materials are in micrometer and nanometer size and instead of using visible light microscopy (poor resolution) we use Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), and Atomic Force Microscopy (AFM) to evaluate their morphology. For determination of the materials' identity: (1) X-Ray Diffraction (XRD) and Selected Area Electron Diffraction (SAED) were used to collect the information of the crystalline/polycrystalline compound; (2) X-Ray Photoelectron Spectroscopy (XPS) was used to collect the information on the oxidation state, chemical

composition and identity of the compound; (3) ^1H and ^{13}C Nuclear Magnetic Resonance (NMR) was used to identify the nature of the compound containing H and C elements, respectively; (4) Line scan and mapping were used to investigate the elemental distribution of the various elements in the composite; (5) Energy-Dispersive X-ray (EDX) and Inductively Coupled Plasma–Optical Emission Spectrometer (ICP-OES) were used to qualify and quantify the various elemental compositions in the composite.

In addition to evaluating the physical properties of the material: (1) Brunauer-Emmett-Teller (BET) instrument was employed to analysis the SSA of the materials; (2) contact angle measurement was performed to understand the wetting behavior of the material.

For electrochemical properties of the material, the following characterizations were used: (1) Battery tester was used to measure the discharging and charging voltages and their respective specific capacities profiles of Li-O₂ battery; (2) Cyclic Voltammetry (CV) measurement was used to measure the energy levels of the semiconductor and capacitance of the material; (3) Linear Sweep Voltammetry (LSV) was used to evaluate the HER performance; (4) Electrochemical Impedance Spectroscopy (EIS) was used to measure the ohmic resistance and charge transfer resistance of the electrochemical processes using a specific electrocatalysts.

3.2 Principles of synthesis methods

3.2.1 Thermal decomposition/Calcination/Carburization

Thermal decomposition, calcination, and carburization processes involve heating of solid materials to high temperature. The temperature, duration of heating, pressure, and ramping rate/cooling rate play a crucial role in bond breaking/formation, morphology/size control, and crystallinity control. When heating at high temperature in air or oxygen, the process is called calcination, and it is usually used to describe oxidation process.^[7] For instance, $\text{Cu}(\text{OH})_2$ forms CuO and H_2O when heated at 500 °C for 4h under air.^[8] Meanwhile in the

absence of air and oxygen, the process is called thermal decomposition. During the decomposition process, thermal energy is needed to separate the chemical bond in the substances. As a result, this process is usually endothermic and the temperature that is sufficient to break the chemical bond is known as the decomposition temperature. ^[9] For example, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O} \rightarrow \text{H}_2 (\text{g}) + 3\text{Cl}_2 (\text{g}) + 6 \text{H}_2\text{O} + \text{Pt metal}$ at temperature above 375 °C under inert condition (*e.g.* He gas). ^[10] For carburization process, it is a heat treatment processes that involve metal or metal oxide in the presence of carbon material and this composite is heated under an inert condition at high temperature. For example, MoO_2/C hybrid forms Mo_2C while releasing H_2O as the side product at a temperature of 700 °C under H_2 atmosphere. ^[11]

3.2.2 Electrochemical deposition

Underpotetnial deposition is an electrochemical deposition method to reduce metal cation (M_1^{n+}) to its metal state (M_1) on another metal (M_2) or same metal (M_1) substrate by applying a positive potential, which is higher than that of the standard reduction potential of $\text{M}_1^{n+}/\text{M}_1$ couple. For example, the standard reduction potential for $\text{Cu}^{2+} + 2\text{e}^- \leftrightarrow \text{Cu} (\text{s})$ is 0.337 V, therefore by applying a potential (*e.g.* 0.345 V) that is higher than 0.337 V, the Cu^{2+} cation can be reduced to Cu onto the another metal substrate (*e.g.* Pt). ^[12-13]

3.2.3 Hydrothermal versus solvothermal reaction

In general, hydrothermal synthesis is defined as a technique involves heating of an aqueous solution at a high temperature to build up high vapor pressure in the reaction vessel (also known as an autoclave) for the fabrication of crystalline materials. By using hydrothermal treatment, we could also synthesize MO from metal precursors via a metal hydroxide intermediate. For example, $\text{M}(\text{X})_n (\text{aq}) + n\text{H}_2\text{O} (\text{l}) \rightarrow \text{M}(\text{OH})_n (\text{s}) + n\text{HX} (\text{aq})$ (X can be Cl^- or NO_3^-) followed by $\text{M}(\text{OH})_n (\text{s}) \rightarrow \text{MO}_{n/2} (\text{s}) + n/2 \text{H}_2\text{O} (\text{l})$. ^[14] In addition, the process of heating an autoclave containing a mixture of carbon-based precursor (*e.g.* glucose) in aqueous solution

is called hydrothermal carbonization (HTC). During HTC process, hydroxyl, carbonyl and other functional groups on the carbon-based material will be decomposed, releasing as a form of gasses molecules (*e.g.* H₂O, CO₂ and etc).^[15] For solvothermal reaction is quite similar to the hydrothermal synthesis. It also uses the stainless steel autoclave to conduct reaction synthesis. The only difference is solvothermal reaction uses a non-aqueous solvent as reaction media instead of an aqueous solution. The size, morphology and crystallinity of the nanostructures could be controlled by altering the reaction conditions (*e.g.* temperature, duration of heating, vapor pressure, nature of the solvent, precursor type, surfactant type, the composition of precursors) of these heating treatments.^[16-18]

3.2.4 Precipitation versus crystallization

The precipitation reaction is a sedimentation process whereby the soluble cations react with the soluble anions, forming insoluble solid particle and precipitate out of the solution. This process is usually fast and the solid particle tends to be amorphous and needed to be treated with calcination process to make it more crystalline. For instance, $\text{CuCl}_2(\text{aq}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Cu}(\text{OH})_2(\text{s}) + 2\text{NaCl}(\text{aq})$,^[8] Cu(OH)₂ is being precipitated out of solution and further heating will convert $\text{Cu}(\text{OH})_2(\text{s}) \rightarrow \text{CuO}(\text{s}) + \text{H}_2\text{O}(\text{l})$.^[8] At this stage the as-obtained CuO is amorphous and after calcination at 500 °C for 4 h under air atmosphere, the amorphous CuO is converted to crystalline CuO.^[8] On the other hand, crystallization using evaporation method is quite similar to precipitation reaction. In this case, this method is a slow process and crystalline solid can be obtained by evaporation. During evaporation, the ratio of solute/solvent increases, resulting in the precipitation of the salt.^[19]

3.2.5 Solvent exfoliation

Exfoliation is a process that separates a layered material into single monolayer sheets. The in-plane chemical bond of the layered material is strong, but the out-

of-plane interaction is weak and the latter is often held by weak van der Waals forces. Exfoliated monolayers are very attractive due to their intrinsic electronic structure and high accessible surface area for chemical or physical reactivity, which give very promising performances to many applications (*e.g.* electrocatalysis,^[20] field effect transistor,^[21] thermoelectric device,^[22] lithium ion battery,^[23] supercapacitor^[24]). There are several ways to exfoliate the layered structure such as: (1) Li intercalation method;^[22, 24] (2) low-temperature annealing under vacuum;^[25] (3) solvent intercalation.^[26] Li intercalation method often has Li as an impurity in the final monolayer product and low-temperature annealing under vacuum is not suitable for material that is unstable upon heating. Most importantly, the yield of these two methods is often too low. Therefore, in this study we use the solvent exfoliation method, which is a simple, scalable and cost-effective technique. For solvent exfoliation, we use the solvent to exfoliate the layered structure, therefore the choice of solvent is very important for this process. As the yield of the monolayer can be optimized if the solvent-layered material has an approximated surface tension of 40 mJ m⁻².^[27] High yield monolayers are desirable in this study as they could be used for several characterizations and HER testing.

3.3 Principles and analyses of characterization techniques

3.3.1 Scanning Electron Microscopy (SEM)/Transmission Electron Microscopy (TEM)

The smallest distance between two points (defined as resolution) a human's eyes can see is about 0.1-0.2 mm. For a visible light microscopy, the best resolution is about 300 nm. However, these resolution is not good enough to see the details on the nanostructured materials. A well-known equation that relates wavelength of the electrons and energy is known as the Louis de Broglie's equation: $\lambda = 1.22/E^{0.5}$ where λ is the wavelength (nm), E is the electron volt (eV). The energy of an electron in the electron microscopy is E = 100 keV, therefore $\lambda = \sim 0.004$ nm and it is lower than the an atom's diameter.

Figure 3.1 (a) Schematic illustration of the basic components in SEM and (b) TEM. Figure 3.1 (a-b) obtained from reference [28].

Figure 3.1a shows the basic components in SEM: (1) electron gun (consists of anode and cathode); (2) condenser and objective lenses; (3) specimen; (4) X-rays, secondary electrons (SE) and backscattering electrons (BSE) detectors; (5) cathode-ray tube (CRT). Figure 3.1b shows major components in the TEM: (1) electron gun; (2) condenser, objective, intermediate, and projector lens; (3) specimen; (4) X-rays detector; (5) fluorescent screen. The electron gun consists of an anode (positively charged plate that attracts electrons) and a cathode (negatively charged plate that repels electrons). When the accelerating voltage is applied, an electron beam radiated from the electron gun migrates from the cathode to the anode. Then this electron beam passes through various type of lenses (*e.g.* objective, condenser, intermediate and projector lenses). These lenses are made of coil wires and when current is applied through the wire coiled, electromagnetic field is generated. [29] This electromagnetic field can control the size of the electron beam. As the size of the electron beam increases, we get better signal to noise ratio. However, the trade-off is that large size beam will result in poor resolution of the image. In SEM, X-rays, SE and BSE are being collected

by their respective detectors and the electrons or X-rays are being amplified as image or spectrum on the CRT. Whereas the image in the TEM measurement is being viewed on the fluorescent screen.

3.3.2 Atomic Force Microscopy (AFM)

Figure 3.2 (a) Schematic illustration of AFM components. (a) Reproduced with permission from ^[30]. Copyright © 2011. The Royal Society of Chemistry. (b) AFM image and (c) height profile of a 2D material.

Figure 3.2a shows that the AFM composes of five main components: (1) a probe has a sharp tip with less than 10 nm diameter. It is located at the end of the cantilever and it measures the force interaction between the probe and material's surface; (2) a piezo scanner moves the sample's position laterally and vertically with respect to the probe; (3) the laser beam coming from the laser diode is reflected off from the cantilever onto the photodetector. (4) the photodetector measures the changes of the laser intensity received from the reflected beam. This reflected beam is caused by the deflection of the cantilever when the probe touches the sample's surface; (5) a feedback control loop is applied to keep a constant interaction between the tip and the sample at all time when the tip scans across the uneven surface. AFM can be performed with three different modes: (1) contact mode – physical contact the surface of the sample with the probe. This physical contact experiences a repulsive van der Waals force. Contact mode is

commonly used for high-resolution imaging. (2) non-contact mode – a tip is maintained a constant distance above the sample. The interaction between tip and sample surface experiences an attractive van der Waals forces. This mode is very useful for height imaging. (3) tapping mode – a probe is in intermittent contact with the sample's surface. Tapping mode is very useful for soft samples (*e.g.* polymer). Figure 3.2b shows a typical AFM images of a single nanosheets with its height profile (Figure 3.2c), showing that the thickness of the nanosheets is about 0.9 nm. There are three types of operation modes for AFM, they are contact mode, non-contact mode and tapping mode. ^[30]

3.3.3 X-Ray Diffraction (XRD)

Figure 3.3 (a) Schematic illustration of the typical constituents in the XRD machine. Figure 3.3a obtained from reference ^[31]. (b) Schematic representation of Bragg diffraction. Figure 3.3b obtained from reference ^[29]. (c) XRD pattern of tungsten (W) substrate.

Figure 3.3a shows that the XRD machine consists of mainly three components: (1) X-ray source provides energy to eject the electron from the sample's surface; (2) sample holder containing a solid sample; (3) X-ray detector received the X-ray that is being scattered from the sample. X-ray is considered to be a wave of an electromagnetic radiation. The electrons in the atom scatter the X-ray wave, causing the X-ray photons to scatter elastically in a periodic lattice. When these scattered waves are in phase and they reinforced one another (constructive interference), diffraction peaks are formed. The diffraction pattern is governed

by the Bragg's equation, i.e. $n\lambda = 2d \sin \theta$ as mentioned earlier in section 3.3.1. However, if these waves cancel out one another (destructive interference), no diffraction peaks will form. Based on the Bragg's equation, the θ obtained from the XRD measurement is a reflection of the d-spacing of the crystal planes (Figure 3.3b). Figure 3.3c shows a XRD pattern obtained from experimental XRD measurement (top graph) can be well matched with the database of W (JCPDS 04-0806). Table 3.1 summarizes the limitations of using XRD technique.

Table 3.1 Limitations of XRD analysis.

Limitations
XRD can only work with crystalline materials, hence glasses and partially crystalline materials cannot be identified using this method.
Phases that comprise less than about 3-5 wt.% (depending on crystal symmetry) of a sample will not be detected.
Mixtures of phases with low symmetry will be difficult to differentiate due to the larger number of diffraction peaks.

3.3.4 X-Ray Photoelectron Spectroscopy (XPS)

Figure 3.4 (a) Schematic illustration of the main components in the XPS instrument. (a) Reproduced with permission from ^[32] Copyright © 2011. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Mechanism of photoelectron spectroscopy. (c) Typical XPS spectrum.

Figure 3.4a presents that the XPS instrument composes of mainly three components: (1) X-ray source provides energy to eject electron from the sample's surface; (2) energy filter collects electrons that are scattered from the sample; (3) detector determines the kinetic energy (KE) of the moving electron. The electron in the atom is being held by the positive nucleus via Columbic attractive force. This Columbic attractive force that holds electron in the atom is called the binding energy (BE), while the amount of energy that is required to overcome this Columbic attractive force is known as the ionization energy. To overcome the BE of the element, the incoming X-ray ($E = h\nu$, where h represents Plank's constant and ν represents the frequency of the X-ray source) must have sufficient energy or higher than that of BE for ionization process to take place. During ionization process, the ejected electrons carry a certain amount of energy, which is known to be $KE = 1/2mv^2$, where m represents the mass of electron and v represents the velocity of electron). Based on the rule of energy conservation, the incoming $h\nu$ (X-ray energy) is equal to the outgoing KE plus BE (Figure 3.4b). We can determine $h\nu$ from the frequency of the X-ray source given and we can measure the KE by the XPS detector, and eventually, the BE of the element can be determined. Figure 3.4c shows a typical XPS spectrum where the y-axis tells us the relative number of electrons (higher the peak means more electrons are being collected), while x-axis tells us the BE of the element. On the extreme left side of the x-axis, a large amount of energy is required to eject the electron from the inner shell (close to the nucleus). Meanwhile, on the utmost right of the x-axis, least amount of energy is required to eject the electron from the outer most shell. The position of the x-axis (BE) tells us the oxidation state of the element or the characteristic of a chemical bond between two atoms. The intensity of the y-axis tells us the composition of that particular species at specified BE with reference to another species at a different BE. The pros and cons of using XPS analysis are summarized in Table 3.2.

Table 3.2 Advantages and disadvantages of XPS analysis. Table 3.2 obtained from reference [33].

Advantages:
Nondestructive
Surface sensitive (10-200 Å)
Elemental sensitivity (parts per 1000)
All elements (except H and He)
Quantitative
Chemical bonding information
Interpretation and theory straightforward
High information content
Disadvantages:
Large analysis area (several mm ²) ^a
Expensive (\$200,000-\$500,000/instrument, \$50-\$500/sample)
High vacuum (10 ⁻⁸ to 10 ⁻¹¹ torr)
Slow (1/2 to 8 hours/sample)
Charging and energy referencing can be a problem
Low resolution (~0.1-1.0 eV)

3.3.5 Inductively Coupled Plasma – Optical Emission Spectrometer (ICP – OES)

Figure 3.5 (a) Schematic illustration of the main components in the ICP-OES instrument. (b) Processes occur during high-temperature heating of the sample solution. (c) Linear calibration plot of various standard concentrations is used to determine concentration in the sample. (a-c) Reproduced with permission from [34] Copyright © 1997. Perkin-Elmer.

Figure 3.5a shows that the ICP-OES instrument consists of mainly six components: (1) nebulizer converts liquid into aerosol, which can be transported to the plasma torch; (2) ICP torch ionizes the atom/ions; (3) radio frequency (RDF) generator provides power for the generation of plasma discharge; (4) transfer optics focuses the radiation onto the entrance slit of the spectrometer; (5) spectrometer differentiates the emission radiation of an element from others; (6) photomultiplier tube (PMT) amplifies the signal produced by a photon.

In the optical emission spectrometry (OES), a sample solution is introduced into to high temperature system. At this high-temperature of approximately 8000°C, the sample solution possesses sufficient thermal energy to undergo desolvation (converts solvent to solid), vaporization (converts solid to gas), atomization (gas atoms/ions are in equilibrium state), ionization (converts atom to ions), and excitation (converts lower energetic state of atom/ion to their higher energetic state). Then these excited ions/atoms will decay to their lower energetic state while emitting electromagnetic wave (Figure 3.5b). This emitted electromagnetic wave (or light) possesses information regarding the nature of the element that exists in the sample. The different element has its own characteristic of wavelength (due to their specific ionization energy). Therefore, we can use OES to measure the light intensity at a specific wavelength to determine the concentration of the element presence. Lastly, we can ascertain the element's concentration in the sample by measuring a set of standard solutions with various concentrations to obtain a calibration line on the plot (intensity versus concentration) as plotted in Figure 3.5c. The advantages of using OES is that high thermal source is used to excite different elements at the same time and we could obtain the emission wavelength of the individual elements nearly at the same time. Therefore, it has the ability of measure different elements presence in the sample concurrently. However, the negative aspect of this phenomena is that interferences wavelength could also be excited, which might overlap with the desired elemental wavelength, leading to inaccurate quantification.

3.3.6 ^1H and ^{13}C Nuclear Magnetic Resonance (NMR)

Figure 3.6 (a) Schematic illustration of the major components in the NMR instrument. (b) Processes take place in NMR instrument. (c) The FID signal is converted to the frequency chart via Fourier transform. (d) The typical range of ^{13}C and ^1H chemical shifts for C and H atoms with various neighboring atoms. Figure 3.6 (a-d) obtained from reference [35].

Figure 3.6a presents an exemplary setup for the NMR instrument, which consists of mainly three components: (1) variable magnetic field generates constant magnetic pulses to the sample; (2) radiofrequency (RDF) oscillator produces signal in the radio frequency range to the sample; (3) RDF detector receives radio frequency signal produced by the sample. Figure 3.6b illustrates the processes occur in the NMR instrument. When there is no magnetic field being applied, all spin states are in the degenerate states. On the other hand, when a magnetic field is being applied on the sample, the energy states of spin state $+1/2$ exhibits a lower energy state (as it is aligned to the applied field, B_0) as compared to the spin state $-1/2$ (situated at higher energy state). When the RF oscillator supplies RF waves to the sample, the sample will absorb this RF wave and the spin state $+1/2$ will get excited to the $-1/2$ spin state, and then relaxes, emitting RF waves that are being detected by the RF detector. The energy that absorbed/emitted by the sample is defined as: $E_{\text{absorbed}} = (E_{-1/2\text{state}} - E_{+1/2\text{state}}) = h\nu$, where h denotes the

Planck's constant and ν_r denotes the frequency emitted by the sample. The emitted RF waves are being collected and represented as the free-induction decay (FID) plot and then the FID plot is Fourier transformed into frequency, as shown in Figure 3.6c. The observed FID is an inference signal between absorbed radiofrequency (ν_{abs}) and emitted radiofrequency (ν_{em}). In practical, we are interested in the chemical shift (δ), which can be derived by the following equation: $\delta = (\nu_{\text{em}} - \nu_{\text{abs}}) / \nu_{\text{abs}}$, which can be reduced to ppm (ppm = Hz/MHz) unit. Figure 3.6d shows the typical position of the ^{13}C and ^1H peaks for various chemical structures. The advantages of using NMR instrument are that we can utilize it for the prediction of the chemical structure of small molecules. At the same time, we can introduce internal standard (internal standard is not reactive towards your sample and the peak of the internal standard does not overlap with your analyte peak) to quantify the amount of analyte presence in the sample. However, there are several limitations: ^[36] (1) the solvent use to dissolve the sample might have peak that overlaps with your analyte peak; (2) if you suppress the solvent signal, the analyte signal will also be suppressed, resulting in structural information lost; (3) this technique often needs to combine with other technique (*e.g.* mass spectrometry) to determine the chemical structure of large molecular analyte (*e.g.* polymer).

3.3.7 Brunauer-Emmett-Teller (BET)

Figure 3.7 (a) Schematic representation of the main components of BET instrument. (b) Schematic representation of the monolayer adsorption represents Langmuir theory and multilayer adsorption represents BET theory. (c) Five types of adsorption isotherms. (c) Reproduced with permission from ^[37]. Copyright © 1940. American Chemical Society.

During sample preparation, samples are required to be degassed in vacuum at high temperatures (temperature is high enough to remove water, without damaging the sample). After the degas process, the samples are transferred into the sample tube, as shown in Figure 3.7a. Then helium (act as blank) and nitrogen (act as adsorbate) are injected into the BET instrument. At low temperature (cooled using liquid N₂) under a partial vacuum state, the nitrogen gas molecules are released into the cell and N₂ molecules are being adsorbed onto the sample surface. During the N₂ adsorption process, there is a change of the relative pressure in the tube, which is lesser than atmospheric pressure. As the pressure

of the N_2 gas increases, the adsorption sites get saturated. At this stage, the measured pressure is called the saturation pressure. After the adsorption sites get saturated, the sample is heated up slowly to remove the N_2 adsorbate from the material surface. Then the data are being collected and plotted as the volume of gas adsorbed against the relative pressure. According to the Langmuir theory for monolayer gas adsorption model (Figure 3.7b), the following assumptions are made: (1) the adsorption energy for adsorbate on all surface site is the same; (2) the concentration of N_2 is directly proportional to the adsorption activity of the material; (3) only monolayer adsorbate is formed. While BET theory (multilayer adsorption model) adds another three more assumptions to that of the Langmuir theory and they are as such: (1) N_2 molecules adsorb on the material surface with infinite layers; (2) the layers of adsorbate does not interact with one another; (3) the theory is applicable for each layer. Figure 3.7c shows five various types of isotherms. Type I isotherm: for material that has pore size diameter < 2 nm. Type II isotherm: At low pressure, N_2 gas fill up the micropores. As the pressure increases, the monolayer starts to form followed by multilayer and finally capillary condensation occur. Type III isotherm: only multilayer adsorbate forms. Type IV and V isotherms: pore diameters between 2–50 nm (for mesoporous materials). The limitations of BET measurements are that it is only applicable to solid sample and it requires a long analysis time if the sample's SSA is too large.

3.3.8 Contact angle measurement

Figure 3.8 (a) Schematic representation of the of the major components in contact angle instrument. (b) Image of different samples with contact angles of 41° and (c) 110° . (a-c) Reproduced with permission from ^[38]. Copyright © 2010. American Chemical Society.

Figure 3.8a shows a simple sketch of a contact angle instrument, which consists of a camera, lens, lamp and a droplet on the flat surface of the sample. When a drop of pure liquid was dripped on the sample surface, the solid-liquid interface experiences an adhesive force. This surface adhesion determines the spreading of the liquid and it is governed by the Young's equation: $\gamma^{SV} - \gamma^{SL} = \gamma^{LV} \cos \theta$, whereby γ^{SV} represents the solid surface free energy, γ^{SL} represents the liquid surface free energy, and γ^{LV} represents the solid-liquid interfacial free energy. The contact angle (θ) equals to zero, representing complete wetting. And, liquid wets the solid surface at $0^\circ < \theta < 90^\circ$, as shown in Figure 3.8b. On the contrary, when the $\theta > 90^\circ$ (Figure 3.8c), the sample is considered to be hydrophobic (nonwetting). The advantage of using contact angle measurement is that it is an inexpensive and a rapid technique for measuring interfacial energy between the material and liquid adsorbate. However, the disadvantage is that the artifact caused by swelling of substrate make the surface chemical information to be ambiguous.

3.3.9 Linear sweep potential (LSV), Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS), Battery Tester

Figure 3.9 (a) Schematic illustration of the typical 2-electrode and 3-electrode systems consist of W.E, C.E, R.E, and electrolyte. (b) A typical LSV curve for HER. (c) CV curves performed at various scan rates. (d) Current density difference at 0.25 V *versus* RHE plotted against various scan rates based on Figure 3.9c. (e) A typical Nyquist plot and (f) voltage versus capacity profile for Li-O₂ battery.

In this section, we are introducing electrochemical measurements (*e.g.* LSV, CV, EIS, and Li-O₂ battery tester) that are used for electrochemical testing in this study. The analyses were carried out using either a 2-electrode system or a 3-electrode system (Figure 3.9a). Figure 3.9b shows a typical LSV curve for HER. When the reduction potential equals to 0 V *versus* reversible hydrogen electrode (RHE), the reaction of HER is at the equilibrium state ($2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2$). After the voltage is being scanned from lower limit (*e.g.* 0 V *versus* RHE) to higher limit (*e.g.* -0.1 V *versus* RHE), a current start to flow and rise to a restriction of -10 mA cm^{-2} . The characteristic of LSV for HER relies on the rate of electron transfer in between of the electrocatalyst and the adsorbate interface. CV is quite similar to LSV. In the case of CV, the voltage is scanned from one limit end (*e.g.* 0.04 V *versus* RHE) to another limit end (*e.g.* 0.44 V *versus* RHE) at various scan rates of 5, 10, 20, 50, 100 mV s^{-1} , as shown in Figure 3.9c. Based on the CV curves in Figure 3.9c, the current density difference (anodic current minus cathodic current) at 0.25 V *versus* RHE is drew against various scan rates to obtain a linear slope (Figure 3.9d). This linear slope represents two times of the double-layer capacitance (C_{dl}). C_{dl} value is an important indication for electrocatalytic activity as it is proportional to the active surface area of the electrocatalyst. To further evaluate the resistance of the electrochemical cell, we conducted EIS measurement on the electrochemical cell. Based on the Ohm's law, resistance (R) can be related to current (I) and potential (E) by the following equation: $R = E/I$. An alternating current (AC) potential is applied across the electrochemical cell and the outgoing current from the cell is being computed as the sum of the sinusoidal functions. As a result, Nyquist plot is being obtained (Figure 3.9e). Then we do fitting on the Nyquist plot to obtain a simplified

Randles circuit model, where R_s represents the electrolyte resistance, C_{dl} symbolizes the double-layer capacitance and R_{ct} symbolizes the charge transfer resistance. This information obtained from the Nyquist diagram is extremely pragmatic in addressing the kinetics properties of the cell reaction. For Li-O₂ battery testing, a voltage scans start from the open circuit voltage (OCV) to a cut-off voltage of 2 V *versus* Li⁺/Li for discharging process (ORR). Meanwhile, in the reverse process, the voltage is being scanned from 2 V *versus* Li⁺/Li to a charging voltage of approximately 3.5 V *versus* Li⁺/Li for OER. Both of the discharging and charging voltages are scanned at a defined current density (*e.g.* 100 mA g⁻¹). The discharging voltage and charging voltage that deviates from the equilibrium potential of Li₂O₂ at 2.96 V *versus* Li⁺/Li is known as the overpotential. The overpotentials are caused by various resistances as mentioned earlier in section 2.2. In the subsequent few chapters, rational-design of electrocatalysts to reduce such overpotentials will be discussed.

3.4 References

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Chapter 4

Improved Wetting of Li_2O_2 on the Metal Oxide/Pt Oxygen Cathodes for High Performance Lithium-Oxygen Batteries

Herein, we develop a unique method for controlling the structure of the Li_2O_2 formed during discharging by improving the wetting behavior of the Li_2O_2 molecules on the oxygen cathode surface. Metal oxide (MO), such as IrO_2 or CuO , is introduced onto the noble metal (e.g. Pt) surface to improve the “wetting” ability towards Li_2O_2 . In the presence of the MO based cathode, Li_2O_2 thin layer is formed. However, in the absence of MO, large Li_2O_2 nanoparticle (NP) is deposited on the oxygen cathode instead. The former provides a shorter electron transport pathway, which enhances the oxygen evolution reaction (OER) kinetics, reduces the charging voltage of Li- O_2 battery with CuO/Pt NSs to 3.73 V at 1 A g^{-1} and thus improves the round-trip efficiency (e.g. 88% at 100 mA g^{-1} and 71% at 1 A g^{-1})

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4.1 Introduction

Currently, researchers become more interested in the rechargeable Li-O₂ batteries as these batteries generally possess a great theoretical specific energy density ($\sim 2\text{--}3 \text{ kWh kg}_{\text{cell}}^{-1}$) in comparison with the Lithium-ion batteries.^[1-5] Tremendous efforts have been made on electrocatalysis involving oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) involving carbons,^[6-10] non-noble metal^[11-14] and noble metal.^[15-20] In spite of all these works were being practically implemented, several challenges still remain. For instance: (1) carbon-related electrodes^[21-23] and electrolytes^[24] are unstable during the discharging process due to the formation of peroxide radical ($\text{O}_2^{\cdot-}$); (2) the formation of irreversible parasitic products^[22, 25] (*e.g.* Li₂CO₃, CH₃CO₂Li, and HCO₂Li) accumulated on the electrode surface might deactivate the electrocatalysts; (3) insulating Li₂O₂ molecules form on the discharged electrode result in poor OER kinetics.^[26]

Recently, many studies have shown that the size and morphology of Li₂O₂ formed on the discharged cathode play important roles in achieving an efficient OER kinetics.^[27-28] Therefore, new strategy is imperatively required to control the structural formation of Li₂O₂ and to minimize the decomposition of carbon-based materials in the Li-O₂ battery by lowering the charging voltage below 4.0 V *versus* Li₊/Li.^[29] For instance, larger Li₂O₂ particles exhibit higher charging voltages as compared to smaller ones.^[28] The former will degrade the carbon-based materials in the Li-O₂ battery,^[22-23] leading to poor cycling stability of Li-O₂ batteries. Previous researches have demonstrated the observation of various Li₂O₂ structures, such as small Li₂O₂ particles,^[30] toroid-like Li₂O₂^[31] and Li₂O₂ thin films,^[26] but the relationship of the Li₂O₂ structure and the surface science of Li₂O₂-catalyst interaction is not definitive. In general, MO possesses ionic characteristic that could form better affinity towards another oxide material via ionic interaction and thus lowering the interfacial energy to form core-shell structure.^[32] In particular, Li₂O₂ tends to form uniform layer on the MO surface as it has a lower interfacial energy between Li₂O₂ and MO as compared to the interfacial energy at the Li₂O₂-noble metal interfaces.^[33] In addition, Fouletier *et al.* have established a relationship between wetting of H₂O molecules and the affinity of O₂ molecules on CuO/Au substrate. It has been demonstrated that O₂ molecules interact better on CuO/Au sample instead of the pure Au sample. As a result, the former exhibits better O₂ activity

as compared to the latter.^[33] Based on these research findings, we believe that the electrochemical performances of Li- O_2 batteries can be enhanced by improving the interactions between catalyst surface and Li_2O_2 molecules. The formation of Li_2O_2 will lower the energy capacity because the Li_2O_2 is electrical insulating in nature. When there are more Li_2O_2 molecules accumulated onto the oxygen cathode surface, the resistance of the overall discharged cathode increases, resulting in large voltage polarization, and thus reduced in energy capacity. To improve the energy capacity, we have grown Pt materials directly on the stainless steel mesh, which provide good electrical contact to reduce the internal resistance and improve the energy capacity.

Herein, we have shown an efficacious way in controlling the structure of the Li_2O_2 by altering the “wetting” property between the electrocatalyst surface and Li_2O_2 molecules. As a result, Li_2O_2 thin layer is obtained for lowering the charging voltage of Li- O_2 battery. In the initial stage of this research, we synthesized IrO_2 nanoparticles (NPs) on Pt nanowires (NWs) and CuO/Pt NWs in comparison with pure Pt NWs through hydrothermal treatment. These as-prepared materials are used for the evaluation of “wetting” ability towards the H_2O and Li_2O_2 molecules. Our preliminary results showed that the cathode containing MO exhibits a better wettability towards H_2O and a better affinity towards Li_2O_2 . This concept has further extended to the fabrication of the three-dimensional (3D) Pt nanosheets (NSs) arrays growing on the stainless steel mesh (SSM) by a seed-assisted growth mechanism via thermal decomposition of Pt solution on SSM. The Fe content in the SSM serves as seeds for the nucleation and the growth of Pt NSs on SSM. It is notable that the direct growth of Pt NSs on SSM has several advantages, such as: (1) provides good electrical contact, which improves the reaction kinetics and increases the discharge/charge capacities; (2) binder-free/carbon-free cathode minimizes the formation of parasitic products and blockage of active sites. Next, we electrodeposit Cu NPs on the Pt NSs. Surprisingly, these Cu NPs are transformed into CuO NPs when exposed to air. The newly formed CuO NPs play an important role when the Li- O_2 battery is discharging, because they act as nucleation sites for Li_2O_2 to

nucleate and grow uniformly on the electrode surface to obtain thin layer structure. This Li_2O_2 thin layer provides a shorter electron transport pathway for OER during charging. We believed that this “wetting” property between substrate and adsorbate is the key in lowering the charging voltage and thus improving the electrochemical performances. Our Li- O_2 battery with CuO/Pt NSs possesses the following excellent electrochemical results: (1) a low charging voltage of 3.73 V at high current density of 1 A g^{-1} ; (2) a high specific capacity of 1648 mAh g^{-1} at 100 mA g^{-1} and 612 mAh g^{-1} at 1 A g^{-1} with a capacity retention of 98% after the 60 cycles; (2) little amount of parasitic products is being detected on the discharged cathode.

4.2 Experimental methods

4.2.1 Chemicals and materials

Chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 99.9%, Alfa Aesar), potassium hydroxide (KOH, 99.99%, Sigma-Aldrich), ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$, 99.8% Sigma-Aldrich), dimethylformamide ($\text{C}_3\text{H}_7\text{NO}$, 99%, Alfa Aesar), sodium hydroxide (NaOH, 99.99%, Sigma-Aldrich), Iridium(III) chloride hydrate ($\text{IrCl}_3 \cdot x\text{H}_2\text{O}$, Reagent grade Sigma-Aldrich), copper(II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 99.999%, Sigma-Aldrich), SSM, 120 mesh, thickness 0.2 mm, ACME Research Support Pte Ltd.), 2-Propanol ($(\text{CH}_3)_2\text{CHOH}$, 99.5%, Sigma-Aldrich), and ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, 99.5%, Sigma-Aldrich).

4.2.2 Synthesis of Pt NWs, IrO_2 /Pt NWs, and CuO/Pt NWs

For the synthesis of Pt NW bundles, 100 mg of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 500 mg of KOH and a mixture of 4 mL ethylene glycol with 6 mL dimethylformamide were added into 25 mL autoclave and stirred for 12h, then heated at 170°C for 8h.^[34] Then 500 μL of as-prepared Pt NWs bundles (10 mg mL^{-1}) was washed with pH 10 NaOH for several times followed by transferring the Pt NWs bundles into the autoclave containing 6 mL of aqueous NaOH (pH 10). Then the autoclave was heated at 120°C for 5 h to separate the Pt NWs bundles into Pt NWs. For the

synthesis of IrO₂/Pt NWs and CuO/Pt NWs, 10 *at%* of the IrCl₃ · xH₂O and 10 *at%* of CuCl₂ · 2H₂O precursors were added into the autoclaves together with the Pt NWs bundles, respectively. The product was rinsed with ethanol and deionized water then stored in ethanol.

4.2.3 Synthesis of network CuO/Pt NSs on stainless steel mesh

The surface of the SSM with dimension 1.5 cm × 1.5 cm × 0.01 cm was cleansed using distilled water and ethanol. The SSM is dried and immersed into a quartz boat (2 cm × 2 cm × 2 cm) containing a mixture of 40 mg of H₂PtCl₆ · 6H₂O in 1 mL of solution (1:1 volume ratio of ethanol:2-propanol). Then the quartz boat was heated to 450 °C at a ramping rate of 20 °C min⁻¹ and dwell at 450 °C for 15 min under 95% Ar:5% H₂ gas environment. Pt NSs grown on the SSM was obtained and dried for 24 h under ambient conditions. Next, this Pt NSs on SSM was used for electrochemical deposition of Cu using a three-electrode setup where Pt NSs on SSM serves as the working electrode (WE), Pt wire serves as counter electrode (CE), and saturated calomel electrode (SCE) serves as the reference electrode (RE). For the electrolyte preparation, 0.05 M of CuSO₄ solute was mixed in 0.5 M H₂SO₄ solvent. The electrodeposition procedure used in this study was according to the previous reported literature.^[35] Then the electrodeposited film was dried in ambient conditions for 24 h. The reddish brown (indication of Cu) films turned black (indication of CuO) in color after 2 min of exposure to air.

4.2.4 Materials characterizations

The samples' shapes and sizes were analyzed using field emission scanning electron microscopy (FESEM, JEOL, JSM-7600F, 5 keV) and transmission electron microscopy (TEM, JEOL Model JEM-2100F, 200 keV) incorporated with scanning transmission electron microscopy (STEM). Elemental contents of samples were characterized using the energy-dispersive X-ray spectroscopy (EDX) mapping. The TEM samples were drop-casted on a carbon film coated

Mo grid. The crystal structures of the materials were analyzed using X-ray diffraction (XRD, Shimadzu XRD-6000, Cu-K α irradiation at $\lambda = 1.5406 \text{ \AA}$). The Brunauer-Emmett Teller (BET) measurements were characterized using a Micromeritics ASAP 2010 analyzer. X-ray photoelectron spectroscopy (XPS) analyses were conducted using a monochromated X-ray source with Al K α radiation ($h\nu = 1486.6 \text{ eV}$) and the collected data were evaluated by the CasaXPS software. The contact angles of the materials were measured using DataPhysics Instrument (OCA 30). The parasitic products were analyzed using ¹H nuclear magnetic resonance (NMR, Bruker 300 NMR spectrometer). For ¹H NMR sample preparation, D₂O was used to dissolve parasitic products and benzene was utilized as the internal standard for the quantification of the parasitic products. The Nyquist plot was obtained using electrochemical impedance spectroscopy (EIS). EIS measurements were conducted by the use of Autolab and the amplitude and frequency range were set to be 10 mV and 10⁵–0.1 Hz, respectively.

4.2.5 Electrochemical measurements

The Li-O₂ cells were assembled in the Ar filled glove box (Unilab, MBRAUM, Germany) with O₂ and H₂O level below 0.1 ppm. The Li-O₂ cells contain ~ 1.0 mg of sample, Li foil as anode and 1 M of lithium triflate (LiCF₃SO₃) in tetraethylene glycol dimethyl ether (TEGDME) electrolyte. Then the Li-O₂ cell was purged with O₂ at 1atm and evaluated using the battery tester (NEWARE model).

4.3 Principle outcomes

4.3.1 Preliminary results for “wetting” study of MO/Pt cathode for Li- O_2 battery

Figure 4.1 (a) TEM images of various cathodes (*e.g.* Pt NWs, IrO₂/Pt NWs, and CuO/Pt NWs) measured during discharging and charging of Li- O_2 battery. (b) Contact angle measurement of Pt NWs, IrO₂/Pt NWs, and CuO/Pt NWs samples on stainless steel foil. (c) Proposed interaction between adsorbates (*e.g.* Li₂O₂ and H₂O) and substrates (*e.g.* Pt NWs, IrO₂/Pt NWs, and CuO/Pt NWs).

For preliminary results, we have fabricated Pt NWs, IrO₂/Pt NWs, and CuO/Pt NWs via hydrothermal method (see the Experimental methods section) for testing the “wetting” ability of H₂O and affinity of Li₂O₂ on MO surface. Figure 4.1a shows that large spherical Li₂O₂ NPs were observed on the Pt NWs electrode under the TEM measurement during discharging of Li- O_2 battery. On the contrary, only Li₂O₂ thin layers were found on the electrodes containing MO (*e.g.* IrO₂/Pt NWs, and CuO/Pt NWs). During charging, Li₂O₂ disappeared for all electrodes, indicating the reversibility of the processes in Li- O_2 batteries. In addition, we have tested the wetting ability of these as-prepared electrodes

towards H₂O by performing a contact angle (θ) measurement (Figure 4.1b). We observed that electrodes containing MO (*e.g.* IrO₂/Pt NWs, and CuO/Pt NWs) has better wetting ($\theta < 10^\circ$) as compared to pure Pt NWs ($\theta > 80^\circ$). Based on these findings, it seems that there is a relationship between the interaction of Li₂O₂–MO and wetting of H₂O–MO. These observations are consistent with previous report as mentioned in section 2.1.1. It is being known that Li₂O₂ and MO have ionic characteristic, while H₂O has covalent characteristic. We proposed that the chemical bonding between Li₂O₂ and MO is ionic interaction, while the chemical bonding between H₂O and MO is hydrogen bonding, as illustrated in Figure 4.1c. These two types of chemical interactions facilitate the orientation of Li₂O₂ molecules and H₂O molecules in such a direction that form layer structure.

Figure 4.2 (a) XPS spectrums of (i) IrO₂/Pt NWs and (ii) CuO/Pt NWs. (b) TEM images with FFT of (i) IrO₂/Pt NWs and (ii) CuO/Pt NWs. (c) Crystal structure representations of (i) IrO₂/Pt NWs with (110)-oriented and (ii) CuO/Pt NWs with (002)-oriented.

To understand the orientation of the adsorbates (*e.g.* Li₂O₂ and H₂O) on the MOs (*e.g.* IrO₂ and CuO) surface, we have carried out several characterizations on the IrO₂/Pt NWs and CuO/Pt NWs samples to investigate the oxidation states and crystal structures of the MOs. First, the XPS measurements were conducted on the samples to verified the oxidation state of the MOs (Figure 4.2a). The characteristic peaks at binding energies of 71.2 and 74.4 eV are corresponding to the Pt (0) state, indicating that the Pt NWs are metallic in nature. The XPS

spectrum for Ir-Pt NWs composite reveals the characteristic peaks at binding energies of 62.4 and 65.0 eV are attributed to the Ir(IV) state, indicating the presence IrO_2 . In addition, the binding energies of 942.2 eV and 960.7 eV are corresponding to Cu(II), indicating the presence of CuO. These results confirmed that we have fabricated IrO_2/Pt and CuO/Pt materials successfully. Next, HRTEM in combine with Fast Fourier Transform (FFT) was used to determine the facet exposed on the MO surface (Figure 4.2b). The d-spacing of the lattice fringes on the IrO_2 NPs is 3.18 Å, which corresponding to an exposed facet of (110). The d-spacing of the lattice fringes on the CuO NPs is 2.12 Å, which corresponding to an exposed facet of (002). The crystal structures of their respective unit cells and exposed planes are illustrated in Figure 4.2c. These two crystal structures have one thing in common, which is the metal to oxygen bonds along the exposed plane are in alternating configuration (*e.g.* M–O–M–O).

Figure 4.3 Simple schematic illustration of the interactions between adsorbates and substrates. The chemical bond lengths are not drawn to scale. (a) Li_2O_2 layer on MO surface; (b) Li_2O_2 NPs on Pt surface; (c) H_2O molecules wet on MO surface; (d) H_2O molecules do not wet well on Pt surface.

These alternating configurations facilitate the orientation of Li_2O_2 and H_2O molecules to form a uniform adsorbate layers on the MO surface via ionic interaction and hydrogen bonding (H-bond), respectively, (see Figure 4.3a and c). In the case of Pt, it has an electronic configuration of Pt: $[\text{Xe}] 4f^{14} 5d^9 6s^1$ and it has the availability of d-orbital to accept negative charges (e.g. peroxide anions) or lone pairs (e.g. O lone pairs on H_2O). However, the cations on the adsorbate (e.g. Li^+ in ionic Li_2O_2) are not favorable to form bond with slightly positive (δ^+) Pt, resulting in the formation of spherical Li_2O_2 NPs. Similar concept can also be applied to H_2O non-wetting on Pt surface (see Figure 4.3b and d).

Figure 4.4 (a) Voltage versus capacity profiles for Li- O_2 batteries with Pt NWs, CuO/Pt NWs, and IrO_2 /Pt NWs samples at 100 mA g^{-1} . (b) Proposed mechanisms of Li_2O_2 thin layer and Li_2O_2 NPs formation in MO/Pt and Pt batteries, respectively.

The electrochemical performances of the Li- O_2 batteries with Pt NWs, CuO/Pt NWs, and IrO_2 /Pt NWs were evaluated in the 1 M $\text{LiCF}_3\text{SO}_3/\text{TEGDME}$ electrolyte at 100 mA g^{-1} . The Pt NWs, CuO/Pt NWs, and IrO_2 /Pt NWs batteries have capacities of 198, 412, and 445 mAh g^{-1} and the charging voltages of 4.20, 3.32, and 3.11 V, respectively (Figure 4.4a). The electrolyte decomposition is taken account in all the discharge/charge profiles. These results show that Li- O_2 batteries containing MO have lower charging voltage in comparison with Li- O_2 battery with pure Pt electrode. The superior electrochemical performances of the former is attributed to the Li_2O_2 thin layer formation during discharging, which provides a shorter electron transport pathway during the charging process, leading to lower of charging voltage as compared to large Li_2O_2 in Pt NWs battery

(Figure 4.4b). However, the rate capability and discharge capacities of these one-dimensional (1D) materials are relatively low, which destroy the advantages of the high theoretical energy of Li- O_2 battery. To resolve this issue, we have rational-designed a 3D electrode to facilitate fast ion flux and provide continuous network for facile electron transport across the electrode surface. In our next study, Pt nanostructures were grown directly on the current collector (*e.g.* stainless steel mesh) to provide good electrical contact. We have chosen CuO over IrO_2 material for this study because the former is cheaper and it is more reasonable for practical implementation. In the following sections we will be discussing on the fabrication of CuO/Pt NSs on SSM for Li- O_2 battery testing.

4.3.2 Synthesis and characterizations of CuO/Pt NSs on SSM for Li- O_2 battery

Figure 4.5 Simple representation of a multi-step synthesis of the CuO/Pt NSs on SSM

Figure 4.5 illustrates the synthesis steps of CuO/Pt NSs grown on SSM. In the first step (thermal decomposition process), SSM were placed in a quartz crucible containing a combination of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, ethanol and 2-propanol. Next, the

crucible was inserted into the furnace and heated up to 450 °C with a dwelling time of 15 min under Ar/H_2 gaseous environment. At such high annealing temperature, all the solvents were evaporated and the Pt precursors were thermally reduced on the SSM, forming NSs arrays structure. In the second step (electrochemical deposition process), the Cu precursor was electrochemically reduced on the Pt NSs surface, forming Cu nanoparticles (NPs) upon the application of voltage. These small Cu NPs (particle size of ~8 nm in diameter) could be oxidized easily and form CuO when exposed to the air. This observation is similar to previously reported literature.^[36] As a result, CuO/Pt NSs hybrid was formed.

Figure 4.6 (a) Top view and (b) side view SEM images of Pt NSs grown on SSM. (c) Low-magnified TEM image and (d) enlarged TEM images with inset of EDX line scan graphs of CuO/Pt NSs sample where red line represents Pt and blue line represents Fe (e) SEM image with inset pore size distribution of CuO/Pt NSs grown on SSM. (f) HRTEM image and (g) SAED pattern of CuO/Pt NSs where red circle represents Pt and blue circle represents Fe

Figure 4.7 (a) Low magnified SEM image of porous Pt NSs grown on SSM. (b) HRTEM image of the Fe root protruding out of Pt NSs.

After the thermal decomposition process, Figure 4.6a and b show the top view and side view SEM images of the Pt NSs grown on SSM. The top-view image shows that the material is sheet-like structure and the approximate thickness of the nanosheets is 20 nm. The cross section-view image indicates that the height of the arrays is around 800 nm. A low magnification SEM image (Figure 4.7a) further proves that the Pts NSs forms a highly porous network structure on the SSM. Then these sheet-like structures were removed from the SSM for TEM characterization (Figure 4.6c). Under the TEM measurement, we observed that these nanosheets (lateral dimension ranging from 150 to 900 nm) appear to have roots protruding out of the nanostructured sheets (denoted by white dotted circle). Further examination of this root is carried out using EDX line scan (Figure 4.6d, inset), showing that Fe content is being detected on the root. Based on this observation, we believed that the Pt NSs are grown from these Fe roots. In addition, the HRTEM image (Figure 4.7b) of the root further proves that the lattice fringes of 2.07 Å is representing the (111) plane of Fe. The XRD pattern (Figure 4.8) reveals that these NSs structures on the SSM are made of Pt (JCPDS PDF No. 04-0802) and it is denoted in red color.

Figure 4.8 XRD patterns of the SSM (bottom, black), Pt NSs on SSM (center, red), and CuO/Pt NSs on SSM (top, blue).

Figure 4.9 SEM images of (a) the smooth SSM and (b) SSM undergoes thermal decomposition. (c) Point EDX analysis marked by black dotted line shows the elemental composition of the smooth SSM surface. (d) Fe seeds are marked by red dotted circle with its corresponding point EDX analysis (marked with red dotted line) shows the presence of elemental Fe.

Figure 4.10 SEM image of (a) Si/SiO₂ substrate and (b) thermal deposition of Pt growth solution with Si/SiO₂ substrate in quartz tube furnace.

It is noticeable that the original SSM have a smooth surface (Figure 4.9a), but after the thermal decomposition process, small seeds are being found on the SSM (Figure 4.9b). These seeds and SSM are being analyzed using the point EDX measurements (Figure 4.9c-d) and the results reveal that the seeds consist of pure Fe element. We believed that these Fe seeds facilitate the growth mechanism of Pt NSs. To verify this hypothesis, we performed the same thermal decomposition process on the smooth Si/SiO₂ substrate (Figure 4.10a), but no sheet-like structure is being observed (Figure 4.10b). This result further confirms that the formation of NSs structure is caused by the existence of Fe seeds on the SSM.

In the subsequent synthesis step, Cu NPs were deposited on the Pt NSs/SSM film via electrochemical deposition using a three-electrode system. After the reaction ends, this film was removed from the Cu electrolyte. At this instant, the film appeared reddish brown, but after 2 min of exposure in air, this film turned black, implying that the Cu NPs have been oxidized to CuO NPs.

Figure 4.11 EDX spectrum of CuO/Pt NSs hybrid.

The elemental composition and elemental distribution of the CuO/Pt NSs material was characterized using EDX analysis (Figure 4.11) and EDX mapping (Figure 4.12a-d), respectively. The EDX measurement (Figure 4.11) reveals that the Cu content presence in the CuO/Pt NSs sample was about 14 *wt%*.

Figure 4.12 (a) HAADF-STEM and (b-d) elemental mapping images of CuO/Pt NSs. (e) Cu 2p spectrum and (f) Pt 4f spectrum of the CuO/Pt NSs sample.

After the electrodeposit CuO NPs onto Pt NS arrays, the surface of the NSs structure become rougher, as shown in Figure 4.6e. Figure 4.6f exhibits a lattice fringes of 2.51 Å and 1.39 Å, which is corresponding to (11-1) plane of CuO and (202) plane of Pt, respectively. The SAED pattern (Figure 4.6g) of the CuO/Pt NSs sample shows a ring-like pattern, implying that the CuO/Pt NSs sample is polycrystalline. The HAADF-STEM (Figure 4.12a) and the EDX mapping (Figure 4.12b-d) images display that O and Cu elements are uniformly distributed on the Pt. The XPS spectrum for CuO/Pt NSs composite reveals the characteristic peaks at 932.0 eV and 952.1 eV are corresponding to Cu 2p_{3/2} and Cu 2p_{1/2}, respectively, indicating the existence of CuO. Figure 4.12e.^[37] The binding energies at 71.2 eV and 74.4 eV in the XPS Pt 4f spectrum (Figure 4.2f) are corresponding to Pt (0) state.^[34]

Figure 4.13 (a-b) Low-magnified SEM images of CuO/Pt NSs and (c) nanoparticles size distribution.

Figure 4.13a-c show the particle size distribution of the CuO NPs on the Pt NSs and the former has a mean diameter of about 8 nm. The XRD pattern (Figure 4.8)

of CuO/Pt NSs on SSM confirms the presence of CuO (JCPDS PDF No. 80-1917) and Pt (JCPDS PDF No. 04-0802) in the sample. It is notable that the CuO (111) plane overlap with the Pt (111) plane at 39.0° – 41.0° , which cannot be differentiated. Fortunately, a sharp peak at 35.7° was observed and it was attributed to the (11–1) plane of CuO. This result was corresponding to the XPS and SAED results shown above. The PSD and SSA profiles of this CuO/Pt NSs network was characterized using N_2 absorption/desorption isotherm. Based on the BJH model (inset in Figure 4.6e), the pore size distribution of this CuO/Pt NSs network has an average pore size of 28 nm and the BET model (Figure 4.14) reveals that the SSAs of CuO/Pt NSs and Pt NSs are $42 \text{ m}^2 \text{ g}^{-1}$ and $33 \text{ m}^2 \text{ g}^{-1}$ respectively. CuO/Pt NSs exhibits a higher SSA over Pt NSs, because the former has a rougher surface compared to the latter.

Figure 4.14 N_2 desorption/adsorption isotherms of the samples and bare stainless steel.

4.3.3 Comparison of the electrochemical performances of CuO/Pt NSs versus Pt NSs batteries

Figure 4.15 (a) Voltage versus capacity profile of Li- O_2 batteries at 1 A g^{-1} consists of Pt NSs and CuO/Pt NSs. (b) Proposed mechanisms of Li_2O_2 NPs and Li_2O_2 thin layer formation in Pt NSs and CuO/Pt NSs batteries, respectively. SEM images of (c) discharged and (d) charged Pt NSs cathode. SEM images of (e) discharged and (f) charged the CuO/Pt NSs cathode.

The electrochemical performance of Li- O_2 batteries with Pt NSs and CuO/Pt NSs were tested in 1 M of $\text{LiCF}_3\text{SO}_3/\text{TEGDME}$ electrolyte at a potential window of 2.0–5.0 V *versus* Li^+/Li . The specific capacities which is computed based on the mass of electrode and the total specific capacities which is measured based on mass of electrode and Li_2O_2 are summarized in Table A.1 respectively (see details in Calculation A.1). The voltage versus capacity profile (Figure 4.15a)

shows that the Li-O₂ battery with CuO/Pt NSs has a specific capacity of 612 mAh g⁻¹ (401 mAh g_{electrode+Li₂O₂}⁻¹) at 1 A g⁻¹, which is 168 mAh g⁻¹ higher than the Li-O₂ battery with Pt NSs at full discharging state. It is being proposed that the superior capacity of CuO/NSs battery might be attributed to the rough surface of the electrode, which provides multiple active sites for ORR, leading to the enhancement of ORR kinetics, and thus increased the discharging capacity. Moreover, the Li-O₂ battery with CuO/Pt NSs displays a higher charging potential of 3.51 V as compared to that of the Li-O₂ battery with Pt NSs (4.45 V). These two charging voltages are defined at a specific capacity of 400 mAh g⁻¹ in Figure 4.15a. These results suggest that the CuO/Pt NSs composite is an efficient OER electrocatalyst.

Figure 4.16 XPS Li 1s spectra of discharged cathode and charged cathode of (a) Pt NSs and (b) CuO/Pt NSs.

To investigate the lithiated products form on the electrode surface during the discharging/charging processes, we performed XPS measurements on the 1st discharged/charged electrodes. The XPS Li 1s spectra (Figure 4.16a and b) reveal that the discharged and charged states of the Li-O₂ batteries with Pt NSs and CuO/Pt NSs are quite similar. Both spectrums at the discharged state exhibit a 54.8 eV binding energy, which is corresponding to Li₂O₂.^[38] During the

charging of Li- O_2 batteries, these Li 1s signals disappear from the spectrums, indicating that the Li_2O_2 product undergoes oxidation process. Most importantly, there is no detection of Li 1s peak at binding energy^[38] of 55.2 e V (corresponds to Li_2CO_3), implying that negligible amount of Li_2CO_3 was found on these carbon-free electrodes.

To evaluate the “wetting” ability of Li_2O_2 on the electrodes (Pt NSs versus CuO/Pt NSs) surface, we examined the discharged/charged electrode using ex-situ SEM. SEM images (Figure 4.15c-d) correspond to different discharging/charging processes labelled in Figure 4.15a. We observed large spherical shape Li_2O_2 NPs on the discharged Pt NSs electrode when the battery was discharged to 2 V. The diameter of the Li_2O_2 NPs is estimated to be 120–200 nm (Figure 4.15c). Upon charging, these Li_2O_2 NPs disappeared (Figure 4.15d), indicating that the Pt NSs battery is rechargeable. On the other hand, we observed Li_2O_2 thin layer on the CuO/Pt NSs electrode surface when the CuO/Pt NSs battery was discharged to 2V (Figure 4.15e). This Li_2O_2 thin layer was made up of small needle-like structure as described in the inset of Figure 4.15e. The Li_2O_2 thin layer has an approximated thickness of 5–25 nm. Similar to Pt NSs battery, upon charging of CuO/Pt NSs battery, the Li_2O_2 needle-like structure disappeared (Figure 4.15f). The appearance/disappearance of Li_2O_2 on the electrodes surface matches with the XPS results in Figure 4.16, indicating that the new structure that forms on the electrode surface during discharging is mainly attributed to Li_2O_2 and not Li_2CO_3 .

Figure 4.17 (a) Voltage versus capacity profile of Li-O₂ batteries at 100 mA g⁻¹, 500 mA g⁻¹, 1 A g⁻¹ (1st cycle) and 1 A g⁻¹ (60th cycle) for Li-O₂ batteries with CuO/Pt NSs. (b) Voltage versus capacity profile of Li-O₂ batteries at 100 mA g⁻¹, 500 mA g⁻¹, 1 A g⁻¹ (1st cycle) and 1 A g⁻¹ (60th cycle) for Li-O₂ batteries with Pt NSs. (c) Charging voltage and specific capacity plot along y-axis against cycle number at 1 A g⁻¹ for CuO/Pt NSs battery. (d) Charging voltage and specific capacity plot along y-axis against cycle number at 1 A g⁻¹ for Pt NSs battery.

The voltage versus capacity profiles (Figure 4.17a and b) of Li-O₂ batteries with CuO/Pt NSs and Pt NSs were conducted at different current densities of 100 mA g⁻¹, 500 mA g⁻¹, and 1 A g⁻¹. The Li-O₂ battery with CuO/Pt NSs has specific capacities of 1648 mAh g⁻¹ (683 mAh g_{electrode+Li₂O₂}⁻¹) at 100 mA g⁻¹, 1050 mAh g⁻¹ (553 mAh g_{electrode+Li₂O₂}⁻¹) at 500 mA g⁻¹, and 612 mAh g⁻¹ (401 mAh g_{electrode+Li₂O₂}⁻¹) at 1 A g⁻¹ (Figure 4.17a). The specific capacity CuO/Pt NSs battery drops slightly to 598 mAh g⁻¹ (524 mAh g_{electrode+Li₂O₂}⁻¹) during prolonged cycling to 60th cycle at 1 A g⁻¹. On the contrary, the Li-O₂ battery with Pt NSs delivers specific capacities of 1259 mAh g⁻¹ (606 mAh g_{electrode+Li₂O₂}⁻¹) at 100 mA g⁻¹, 773 mAh g⁻¹ (465 mAh g_{electrode+Li₂O₂}⁻¹) at 500 mA g⁻¹, and 448 mAh g⁻¹ (324 mAh g_{electrode+Li₂O₂}⁻¹) at 1 A g⁻¹ (Figure 4.17b). The specific capacity of the Pt NSs battery drops significantly to 195 mAh g⁻¹ (167 mAh g_{electrode+Li₂O₂}⁻¹) during the 60th cycle. To evaluate the round-trip efficiencies of the Li-O₂ batteries, we

divided the discharging voltage by charging voltage defined at a specific capacity of 300 mAh g⁻¹. The Li-O₂ battery with CuO/Pt NSs exhibits round-trip efficiencies of 88% and 71% at 100 mA g⁻¹ and 1 A g⁻¹, respectively. In particular, this round-trip efficiency at 1 A g⁻¹ is higher than that of the round-trip efficiency in Pt NSs battery (*e.g.* 54% at 1 A g⁻¹). Amazingly, after prolonged cycling at 60th cycle, the CuO/Pt NSs battery can deliver a round-trip efficiency of 83% at 100 mA g⁻¹, which is apparently greater than that of round-trip efficiency in Pt NSs battery (*e.g.* 45% at 1 A g⁻¹). This round-trip efficiency of the CuO/Pt NSs battery has surpassed the previous literature (*e.g.* Ru/TiSi nanonet^[13] 70% at 200 mA g⁻¹, CNT@RuO₂ composite^[18] 79% at 100 mA g⁻¹ and pure carbon^[15] 57% at 85 mA g⁻¹.)

For durability testing of Li-O₂ batteries, both the CuO/Pt NSs and Pt NSs batteries are being discharged/charged at 1 A g⁻¹ and their respective specific capacities and charging voltages in are plotted along the y-axis versus the cycle number in x-axis (see Figure 4.17c and d). The Li-O₂ battery with charging voltage above 4.0 V often exhibits poor cycle stability due to electrolyte degradation.^[39] Therefore, the Li-O₂ battery that able to charge up below 4.0V is desirable. Figure 4.17c shows that the Li-O₂ battery with CuO/Pt NSs has a specific capacity of 612 mAh g⁻¹ at 1 A g⁻¹ during the 54th cycle. In addition, this CuO/Pt battery could achieve a high capacity retention of 98% and low charging voltages (*e.g.* 3.73 V at 1st cycle and 3.95 V at 60th cycle). On the contrary, the Pt NSs battery displays a specific capacity of 160 mAh g⁻¹ with a capacity retention of 64% during the 60th cycle. A sharp drop in capacity is being observed after 30 cycles (Figure 4.17d). We believe that such significant decay of specific capacity in Pt NSs battery is a result of the accumulation of parasitic products across the electrode surface, which deactivate the catalyst. In addition, the Pt NSs battery has a charging voltages of 4.48 V (1st cycle) and 5.00 V (60th cycle). It is notable that the CuO/Pt NSs battery has a much lower charging voltage as compared to Pt NSs battery during the 60th cycle. This result suggests that CuO/Pt Ns is a better OER catalyst as compared to Pt NSs.

Figure 4.18 Nyquist plot of Pt NSs and CuO/Pt NSs batteries at 1st full discharge under 1 atm pressure of O_2 .

Then EIS measurement was conducted on the discharged Li- O_2 under 1 atm pressure of O_2 to obtain the Nyquist plot, as shown in Figure 4.18. The Nyquist plot exhibits that the series resistances of CuO/Pt NSs battery and Pt NSs battery are 144 ohm and 83 ohm, respectively. This result suggests that the Pt NSs battery with a lower series resistance is more electrical conducting as compared to CuO/Pt NSs battery. In electrocatalysis, the charge-transfer resistance (represented by the semi-circles in the high frequency region) is an indicator for predicting the reaction kinetics. For instance, the charge-transfer resistances of the CuO/Pt NSs battery and Pt NSs battery are 219 ohm and 337 ohm, respectively. The CuO/Pt NSs battery displays a lower charge-transfer resistance, which indicates that it has a better electron transfer rate between the electrode surface and redox species in the solution at the electrode-electrolyte interface as compared to Pt NSs battery. We believe that such low charge-transfer resistance in the CuO/Pt NSs battery might be due to the formation of Li_2O_2 thin layer, which provides a short charge transport pathway during the charge-transfer process. As a result, the OER kinetics in CuO/Pt NSs battery improves, and thus lowered the charging voltage, as depicted in Figure 4.17a and c.

Figure 4.19 ^1H NMR spectra of (a-b) Pt NSs and (c-d) CuO/Pt NSs batteries at discharged and charged states.

We performed ^1H NMR analyses using benzene as an internal standard to investigate the content of lithium alkyl carbonate products formed on the discharged/charged electrodes. The parasitic products being detected are mainly HCO_2Li and $\text{CH}_3\text{CO}_2\text{Li}$. The chemical shifts at 1.82 ppm and 8.37 ppm are corresponding to $\text{CH}_3\text{CO}_2\text{Li}$ and HCO_2Li , respectively.^[40] Figure 4.19a shows that 0.85 μmol of $\text{CH}_3\text{CO}_2\text{Li}$ and 1.28 μmol of HCO_2Li were found on the discharged Pt NSs electrode. Figure 4.19b exhibits that the ^1H peaks of HCO_2Li and $\text{CH}_3\text{CO}_2\text{Li}$ disappeared on the charged Pt NSs electrode, which is attributed to the oxidation of Li_2O_2 . On the contrary, 1.51 μmol of HCO_2Li can be found on the discharged CuO/Pt NSs electrode (Figure 4.19c) and in the subsequent charging process the ^1H signals of $\text{CH}_3\text{CO}_2\text{Li}$ and HCO_2Li disappeared (Figure 4.19d). These results show that the quantity of parasitic products in the CuO/Pt

NSs battery are lesser in comparison with the Pt NSs battery. We believe that such low content of parasitic products in the CuO/Pt NSs battery might be one of the possible reason that leads to superior electrochemical performances, such as low charging voltage and long cycle life.

Figure 4.15b presents the proposed mechanisms of Li_2O_2 formation on Pt NSs and CuO/Pt NSs electrodes. During the discharging process, CuO NPs on Pt NSs surface serves as multiple nucleation sites for Li_2O_2 to nucleate and grow uniformly on the electrode surface, forming Li_2O_2 thin layer. The formation of CuO/Pt NSs core and Li_2O_2 shell indicates that the Li_2O_2 “wet” well on the CuO/Pt NSs surface as the interfacial energy of Li_2O_2 -CuO/Pt interaction is relatively low. This Li_2O_2 thin shell on the CuO/Pt NSs surface provides a shorter electron transport pathway during the OER, and thus lowered the charging voltage (compared the charging voltages of CuO/Pt NSs battery and Pt NSs battery in Figure 4.15a). On the contrary, large Li_2O_2 NPs form on the Pt NSs electrode surface due to the lack of nucleation sites, leading to local nucleation of Li_2O_2 on Pt NSs surface. The Li_2O_2 does not seem to “wet” well on the Pt surface, because the interfacial energy between the Li_2O_2 and Pt NSs is relatively high. Therefore, the Li_2O_2 -Pt interaction is unfavorable. This large Li_2O_2 NPs on the Pt NSs electrode has a longer electron transport pathway, as illustrated in Figure 4.15b. As a result, the high charging voltage is obtained in Pt NSs battery containing large Li_2O_2 NPs (compare the charging voltages of CuO/Pt NSs battery and Pt NSs battery in Figure 4.15a). The morphology of the Li_2O_2 formed during discharging plays a crucial role in establishing specific pathways for electron movements. For instance, shorter electron transport pathway leads to the lowering of charging voltages in Li- O_2 battery. Such low charging voltage is very important in Li- O_2 battery as it will minimize the electrolyte degradation and minimize the parasitic products form. Once the parasitic products could be minimized the cycle life of the Li- O_2 battery can be improved.

4.4 Conclusions

In summary, we have tested the hypothesis of wetting of Li_2O_2 on MO (*e.g.* IrO_2 and CuO) on Pt electrode by two different synthesis approaches. First the IrO_2/Pt NWs, CuO/Pt NWs and Pt NWs were synthesized via hydrothermal treatment. The Li- O_2 battery with Pt NWs act as a control experiment. In the presence of MO (*e.g.* IrO_2 and CuO) on Pt NWs, H_2O and Li_2O_2 molecules “wet” better on the MO/Pt surface than on the Pt surface. We proposed that the alternating configuration (*e.g.* M-O-M-O) in the crystal structure of the MO provides hydrogen bonding and ionic interaction towards H_2O and Li_2O_2 molecules, respectively. Such alternating configuration could orientate the adsorbates (*e.g.* H_2O or Li_2O_2) in the direction that forms layer structure on the MO/Pt electrode surface. Based on our observation, it seems that there is a relationship between wetting of H_2O on MO and affinity of Li_2O_2 on MO. MO/Pt tends to have better “wetting” and strong affinity towards H_2O and Li_2O_2 as compared to pure Pt. To enhance the specific capacity of the Li- O_2 battery, we further modified the electrode into a 3D network structure (*e.g.* Pt NSs arrays grown on SSM through thermal decomposition process). This 3D network structure has several structural advantages: (1) provides good electrical contact between electrocatalysts and current collector; (2) provides facile electron transport across the electrode; (3) improve the ionic flux. Next, we electrodeposited Cu NPs onto the Pt NSs and the Cu get oxidized into CuO in air, forming CuO/Pt NSs composite. The CuO/Pt NSs battery has a high specific capacity of 1648 mAh g^{-1} ($683 \text{ mAh g}_{\text{electrode}+\text{Li}_2\text{O}_2}^{-1}$) at 100 mA g^{-1} . In addition, the formation of Li_2O_2 thin layer improves the OER kinetics and lowers down the charging potential to 3.73 V. We believe that the introducing MO onto noble metal surface can improve the affinity towards Li_2O_2 , which is the key to achieve low charging voltage. We envisage that our research will enlighten others to consider the “wetting” property between the adsorbate and catalyst surface for any other energy-related electrocatalysis.

4.5 References

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Chapter 5

Microporous Mo₂C for Efficient Hydrogen Evolution

Novel three-dimensional hierarchical porous molybdenum carbide (3DHP-Mo₂C) has been constructed from porous nitrogen-doped carbon framework (PNDCF) as an efficient and inexpensive HER electrocatalyst. A unique template-assisted strategy has been introduced to synthesize 3DHP-Mo₂C by carburizing Mo-PNDCF hybrid. The as-obtained 3DHP-Mo₂C material exhibits several structural merits, including large SSA (521 m² g⁻¹), continuous network structure and porous nanostructure with majority of pore size being 11 Å diameter. These beneficial textures provide large surface active sites, reduce charge transfer resistance as well as facilitate fast electron transfer and proton mass transport during HER. As an efficient electrocatalyst for HER, the 3DHP-Mo₂C electrocatalyst exhibits a small overpotential of 37 mV with a high exchange current density at 2.8×10^{-1} mA cm⁻² and an excellent electrochemical stability.

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5.1 Introduction

Hydrogen fuel currently has become more popular because of its large specific energy density (143 MJ kg⁻¹) over other energy-related devices.^[1] Hydrogen gas can be generated through water electrolysis and this process is also known as the hydrogen evolution reaction (HER).^[2] The HER occurs at a potential of 0 V *versus* RHE, whereby the reaction is $2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2$.^[3] Pt is considered to be an efficient electrocatalyst as it has an HER overpotential close to zero, resulting in significant improvement of energy efficiency.^[4] However, there are still some issues required to be addressed: (1) Pt material is scarce and high-priced, which restrain its practical application;^[5] (2) insufficient catalytic sites for HER leading to poor energy efficiency;^[6] (3) some electrocatalysts exhibit poor chemical stability in harsh acidic conditions.^[7] Despite all these challenges, tremendous efforts have been made to find an alternative efficient and low-cost material for HER.^[8-12]

Recently, studies have revealed that Mo carbide material has similar electronic property as Pt, making it a promising material for HER.^[12-13] In addition, proper designing of Mo₂C nanostructures (*e.g.* Mo₂C/CNT and Mo₂C NWs) could enhance the HER performances.^[14-15] For an idea electrocatalyst, high electrical conductivity of the material is necessitated in minimizing energy losses from ohmic polarization. Also, a huge SSA is needed to provide extra reaction sites for HER.^[16] Three-dimensional (3D) porous structures have attracted a lot of attention as its unique structure provides an efficient pathway for mass transportation of the redox species from the electrolyte to the electrocatalyst surface.^[17] This beneficial property of the 3D porous material makes it more advantageous towards universal applications involving electrochemical reactions.^[18-20] Moreover, Ito *et al.* have demonstrated that by chemically doping (*e.g.* N, and S) in carbon sample, the electronic structure of the material could be optimized for efficient HER.^[21] Several studies have also indicated that by embedding metal in N-doped carbon material, the hybrid material exhibits synergistic effect towards HER and therefore the HER performances could be

improved.^[22-23] Despite all these efforts, rational-design of 3D porous Mo₂C with high SSA and small PSD has not been established for HER.

In this study, we fabricate a 3D hierarchical porous Mo₂C framework (3DHP-Mo₂C) through the template-assisted approach. For the first time, we observe the fabrication of nitrogen-doped carbon framework (PNDCF) via solvothermal treatment on a solution containing pyridine and Na. This PNDCF possesses a huge SSA of 2330 m² g⁻¹ and it is used as template for synthesizing 3DHP-Mo₂C. The as-prepared 3DHP-Mo₂C electrocatalyst exhibits a dominant pore size of 11 Å in diameter. These micropores in the 3DHP-Mo₂C sample exhibits a low operating overpotential of 97 mV at 10 mA cm⁻², which is much lower than that of the existing Mo-based material (Table A.2). To investigate the pore size effect for HER, we have also synthesized mesoporous Mo₂C materials for control experiments. For example, the mesoporous Mo₂C materials are interconnected Mo₂C/nitrogen-doped carbon nanotubes (I-Mo₂C/NCNT) and interconnected Mo₂C/carbon nanotubes (I-Mo₂C/CNT). The results suggest that Mo₂C with dominant micropores has lower operating potential as compared to Mo₂C with dominant mesopores. We believe that the former promotes fast charge transport of redox species from the electrolyte to catalyst surface, leading to rapid reaction kinetics and thus reduced the HER operating potential.

5.2 Experimental methods

5.2.1 Chemicals and materials

Sodium (Na, 99.9%, Sigma-Aldrich), pyridine (C₅H₅N, 99.9%, Sigma-Aldrich), carbon nanotube (CNT, Chengdu Organic Chemical), ammonium molybdate ((NH₄)₂MoO₄, 99.98%, Sigma-Aldrich), Nafion solution (0.5 wt%, Sigma-Aldrich), ethanol (CH₃CH₂OH, 99.5%, Sigma-Aldrich), commercial Pt on Vulcan XC-72 (Pt/C, 20 wt%, Premetek), sulfuric acid (H₂SO₄, 99.999%, Sigma-Aldrich), phosphate buffer solution (PBS, 0.1 M, Sigma-Aldrich), and potassium hydroxide (KOH, 90%, Sigma-Aldrich)

5.2.2 Synthesis of carbon-based materials

For the fabrication of PND CF material, 10 mL of pyridine and 4 g of Na were added in an autoclave and reaction vessel was heated to 250 °C for 24 h. After the reaction was completed, a solid product was obtained and annealed at 700 °C for 30 min under inert condition (*e.g.* Ar gas). Then the solid product was rinsed with deionized H₂O to neutralize the sample to pH ~7. The fabrication of NCNT sample through hydrothermal treatment was according to reported literature,^[24] and bare CNT was purchased from Chengdu Organic Chemicals. Lastly, all the samples were dried in vacuum oven at 60 °C for 24 h.

5.2.3 Synthesis of Mo₂C electrocatalysts

In general, 120 mg of carbon-based samples (*e.g.* PND CF, NCNT and CNT) and 100 mg of (NH₄)₂MoO₄ were mixed in distilled water and heated at 100 °C until all the solvent was evaporated. Then the solid powder of Mo/carbon-based composites were annealed to 700 °C at an increasing rate of 10 °C min⁻¹ and dwell for 2 h under the 5% H₂:95%Ar atmosphere. Lastly, the final products were rinsed with deionized H₂O followed by ethanol, and then dried in vacuum oven at 60 °C for 24 h.

5.2.4 Materials characterizations

The shapes and sizes of the samples were analyzed using field emission scanning electron microscopy (FESEM, JEOL, JSM-7600F, 5 keV) and transmission electron microscopy (TEM, JEOL Model JEM-2100F, 200 keV) incorporated with scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDX). The crystal structure of the materials was analyzed using X-ray diffraction (XRD, Shimadzu thin film diffractometer with Cu K α irradiation at $\lambda = 1.5406 \text{ \AA}$). The N₂ adsorption-desorption isotherm measurements were characterized using ASAP Tri-star II 3020 model instrument. The X-ray photoelectron spectroscopy (XPS, VG Escalab 250 spectrometer) were conducted using Al K α anode ($h\nu = 1486.6 \text{ eV}$). The amount of Mo₂C

loading on carbon-based materials was determined using Carbon Hydrogen Nitrogen Sulfur (CHNS) elemental analyzer (Elementar Vario Micro Cube) in combine with inductively coupled plasma–optical emission spectrometer (ICP-OES, Dual view Optima 5300 DV).

5.2.5 Electrochemical measurements

The HER performance was conducted using a three-electrode setup. This setup consists of a graphite rod as counter electrode (C.E), saturated calomel electrode (SCE) as reference electrode (R.E), and glassy carbon (3 mm in diameter) as working electrode (W.E). The catalyst slurry was formulated by mixing 4 mg of sample with 0.1 mL H₂O, 0.9 mL ethanol and 20 μ L (0.5 wt% of Nafion solution) and then the slurry was sonicated for 30 min. Next, 5 μ L of the slurry (equivalent to mass loading of 0.28 mg cm⁻²) was drop-casted onto the W.E and dried at ambient conditions. Then HER measurements were conducted using a linear sweep voltammetry and potential was scanned at a range of 0.1 to -0.3 V *versus* RHE with a scan rate of 2 mV s⁻¹ in various types of electrolyte, for examples: 1 M KOH, 0.5 M H₂SO₄, and 0.1 M phosphate buffer solutions. Cyclic voltammetry (CV) analyses were performed at various scan rates of 5, 10, 20, 50, 100 mV s⁻¹ at a potential range of 0.04–0.44 *versus* RHE. All the data were calibrated to RHE and compensated by ohmic losses. Electrochemical impedance spectroscopy (EIS) was performed at distinct potentials (*e.g.* 10, 100, 200 mV) at a frequency window of 0.1–10⁵ Hz.

5.3 Principle outcomes

5.3.1 Synthesis and characterizations of porous Mo₂C materials

Figure 5.1 Simple representation of growth processes of 3DHP-Mo₂C. (I): Solvothermal treatment of a mixture containing pyridine and sodium (Na) to obtained PNDCF. (II): Evaporation of the aqueous mixture (containing Mo and PNDCF precursors) to obtain Mo-PNDCF hybrid. (III): Carburization of Mo-PNDCF hybrid to form 3DHP-Mo₂C product.

Figure 5.1 illustrates the growth mechanisms of the 3DHP-Mo₂C. In the first step, the PNDCF sample was mixed with Na and pyridine precursors followed by solvothermal treatment at 250 °C. It is notable that metal Na(0) state act as an initiator for polymerization of pyridine at high temperature. These polymers are cross-linked together to form the 3D porous network. Meanwhile, the oxidized Na(+1) ions could also facilitate coordination of the polymers, forming interconnected structure.^[25] Next, the as-prepared Na/polymers composite underwent thermal decomposition process to form Na/N-doped C network followed by removal of Na residual through rinsing the sample with water until the pH of the solution reached 7. In the second step, the as-obtained PNDCF was mixed in an aqueous containing (NH₄)₂MoO₄, then heat was applied to remove the water solvent at 100 °C, forming Mo-PNDCF composite. In the last step, the Mo-PNDCF composite underwent carburization process at 700 °C in H₂/Ar gas atmosphere to obtain the final product, 3DHP-Mo₂C. For control experiments purpose, other porous samples, such as I-Mo₂C/CNT and I-Mo₂C/NCNT were

also being synthesized (see experimental methods for details) for further analyses and HER testing.

Figure 5.2 (a) XRD pattern, (b) low-magnified SEM image, (c) high-magnified SEM image, (d) TEM image, (e) HRTEM image, (f) HAADF-STEM image, and elemental mappings of 3DHP-Mo₂C sample.

Figure 5.3 XRD patterns of (a) I-Mo₂C/NCNT, (b) I-Mo₂C/CNT, and (c) PNDCF samples.

Figure 5.2a and 5.3a reveal the XRD patterns of the 3DHP-Mo₂C and Mo₂C/NCNT samples, respectively. Both of the samples have the diffraction peaks of 34.3, 37.7, 39.3, 51.9, 61.5, 69.1, 72.4 and 74.5°, which are corresponding to hexagonal β -Mo₂C (JCPDS No. 35-0787). However, the

majority of peaks in XRD pattern of I-Mo₂C/CNT material (Figure 5.3b) are attributed to orthorhombic Mo₂C (JCPDS 31-0871). Based on the XRD results, we have successfully fabricated Mo₂C material. Moreover, the XRD pattern of the PND CF template (Figure 5.3c) displays a wide peak at 30.0°, representing that the PND CF composites is an amorphous carbon. [26-27] The elemental contents in the samples were investigated using ICP-OES and CHNS elemental analyser. It is notable that the Mo₂C content in the all the carbon templates are relatively similar and they are being tabulated to be ~30 wt% (see details in Calculation A.2), and the N content in the carbon samples are about 0.6-0.7 wt% (see Table A.3). Moreover, the XPS N 1s spectrums (Figure 5.4a-b) for both 3DHP-Mo₂C and I-Mo₂C/NCNT samples have a clear signal at binding energy of 398.3 eV, which is corresponding to the C–N bond in the N-doped carbon composite. [28]

Figure 5.4 XPS N 1s spectrums of (a) 3DHP-Mo₂C and (b) I-Mo₂C/NCNT samples.

Figure 5.5 (a) SEM image and (b) TEM image of PND CF sample.

Following on, we studied the shapes and sizes of the all the samples using TEM and SEM measurements. The SEM and TEM images (Figure 5.5a-b) show that the PNDCF sample composed of a porous network structure, containing a pore size range between ~ 1 – 42 nm in width. This surface morphology of PNDCF are quite similar to that of 3DHP-Mo₂C, as illustrated in the SEM and TEM images with different magnifications (Figure 5.2b-d). These results suggest that the PNDCF material has an excellent structural stability towards high temperature carburization process. An enlarged TEM image (Figure 5.2e) of the 3DHP-Mo₂C sample reveals that the small Mo₂C crystal (~ 2 nm in diameter) is encapsulated in the PNDCF matrix. This tiny Mo₂C crystal has a d-spacing of 0.26 nm, which is attributed to the (100) atomic plane of β -Mo₂C. Moreover, the pore size of on the 3DHP-Mo₂C sample is estimated to be 1.9 nm. The HAADF-STEM image and EDX mapping images (Figure 5.2f) of 3DHP-Mo₂C reveals that the Mo, N and C elements are evenly dispersed on the material.

Figure 5.6 SEM images of (a-b) I-Mo₂C/CNT and (c-d) I-Mo₂C/NCNT samples.

Figure 5.7 TEM and HRTEM images of (a-c) I-Mo₂C/CNT and (d-f) I-Mo₂C/NCNT.

Figure 5.8 HAADF images and EDX elemental mapping images of (a-c) I-Mo₂C/CNT and (d-g) I-Mo₂C/NCNT samples

In this study, we have also fabricated control samples (*e.g.* I-Mo₂C/CNT and I-Mo₂C/NCNT) and their morphologies were delineated using SEM and TEM measurements. The SEM images (Figure 5.6a-d) show that the I-Mo₂C/CNT and I-Mo₂C/NCNT samples are interconnected, forming a porous network structure. The TEM images (Figure 5.7a-f) show that the Mo₂C nanocrystals are estimated 2-3 nm in diameter and they are evenly scattered on the CNT substrate without showing obvious aggregation of particles. Moreover, the HAADF images and

EDX mapping images (Figure 5.8a-g) of these two samples show that the elements (*e.g.* Mo, C and N) are uniformly distributed on the materials.

Figure 5.9 (a) N₂ desorption-adsorption isotherm, (b) PSD, and (c) CPV profiles of the 3DHP-Mo₂C sample.

Figure 5.10 (a) N₂ adsorption and desorption isotherm, (d) PSD, and (g) CPV profiles of I-Mo₂C/CNT (b) N₂ adsorption and desorption isotherm, (e) PSD, and (h) CPV profiles of I-Mo₂C/NCNT. (c) N₂ adsorption and desorption isotherm, (f) PSD, and (i) CPV profiles of PND CF.

The SSAs and PSDs profiles of the Mo₂C samples were examined using N₂ adsorption/desorption isothermal measurements. Figure 5.9a and 5.10a-c show that the 3DHP-Mo₂C, I-Mo₂C/NCNT, I-Mo₂C/CNT and PND CF materials have SSAs of 302, 109, 101 and 2330 m² g⁻¹, respectively. While, Figure 5.9b-c and 5.10d-i reveal that the 3DHP-Mo₂C, I-Mo₂C/NCNT, I-Mo₂C/CNT and PND CF materials have pore size distributions of 11, 287, 340 and 13 Å, respectively. There are mainly three types pore sizes, which can be categorized as: (1) micropores (pore width <20 Å); (2) mesopores (pore width between 50 and 500 Å); (3) macropores (pore width >600 Å), as illustrated in Figure 5.9b. Herein, the as-synthesized materials consist of two different types of pores and they are the microporous Mo₂C (*e.g.* 3DHP-Mo₂C) and mesoporous Mo₂C (*e.g.* I-Mo₂C/NCNT and I-Mo₂C/CNT).

5.3.2 Comparison of the HER performances of microporous Mo₂C versus mesoporous Mo₂C electrocatalysts

Figure 5.11 Polarization curves of 3DHP-Mo₂C electrocatalyst with various Mo₂C wt% loading on the PND CF support in 0.5 M H₂SO₄ solution. The content of Mo₂C wt% on the PND CF support was determined using ICP-OES elemental analysis (see details in Calculation A.2).

Figure 5.12 (a) Polarization curves of I-Mo₂C/CNT, I-Mo₂C/NCNT, 3DHP-Mo₂C, carbon supports (CNT, NCNT and PND CF), and Pt/C electrocatalysts at 2 mV s⁻¹ in 0.5 M H₂SO₄. (b) Tafel plots of I-Mo₂C/CNT, I-Mo₂C/NCNT, 3DHP-Mo₂C, and Pt/C samples. (c) Schematic representation of the polarization (η) between microporous and mesoporous materials. (d) Schematic representation of the proton mass transport in microporous and mesoporous materials.

The HER performances of the samples were examined in three different media: (1) 0.5 M H₂SO₄ (pH 0); (2) 0.1 M phosphate buffer (pH ~7); (3) 1 M KOH (pH 14). For comparison purpose, the Pt/C and various carbon templates (*e.g.* PND CF, NCNT, and CNT) were also evaluated. It is notable that the 3DHP-Mo₂C sample with a ~30 wt% of Mo₂C loading has an optimal HER electrocatalytic activity, as depicted in Figure 5.11. For consistency testing, the amount of Mo₂C loading on the I-Mo₂C/NCNT and I-Mo₂C/CNT samples are similar to that of 3DHP-Mo₂C (~30 wt%).

Figure 5.12a and 5.12b show that the LSV curve and Tafel plot of the Pt/C electrode has an excellent HER activity, which consist of a low onset potential (*e.g.* close to 0 mV) and a low Tafel slope (*e.g.* 32 mV dec⁻¹), respectively. These values are in agreement with the reported ones.^[29] On the contrary, the LSV

curves (Figure 5.12a) of the carbon templates show expected poor HER results in comparison with their respective Mo₂C-based samples. This exceptional HER activity of Mo₂C could be due to the availability of metal (*e.g.* Mo) d-orbital, which provides active sites for HER.

The Mo₂C-based materials of 3DHP-Mo₂C, I-Mo₂C/NCNT, and I-Mo₂C/CNT have operating overpotentials of 97, 148, and 160 mV at 10 mA cm⁻², respectively. Among them, the 3DHP-Mo₂C sample has the lowest operating overpotential in comparison with the rest of the Mo₂C-based samples. This result suggests that the 3DHP-Mo₂C sample requires less energy to drive the HER forward and it is considered as an efficient catalyst. Figure 5.12b shows a typical Tafel plots (voltage versus Log I) where the slope of this graph is known as the Tafel slope. The value of Tafel slope reflects on the mechanisms of the HER. For examples, in acidic solution, the HER has three types of mechanisms: ^[30] (1) Volmer-mechanism ($\text{H}_3\text{O}^+ + \text{e}^- + \text{catalyst} \rightarrow \text{catalyst-H} + \text{H}_2\text{O}$); (2) Tafel-mechanism ($\text{catalyst-H} + \text{catalyst-H} \rightarrow 2 \times \text{catalysts} + \text{H}_2$); (3) Heyrovsky-mechanism ($\text{H}_3\text{O}^+ + \text{e}^- + \text{catalyst-H} \rightarrow \text{catalyst} + \text{H}_2 + \text{H}_2\text{O}$). The 3DHP-Mo₂C, I-Mo₂C/NCNT and I-Mo₂C/CNT samples have the Tafel slopes of 60 mV dec⁻¹ ($\eta = 35\text{-}104$ mV), 71 mV dec⁻¹ ($\eta = 50\text{-}99$ mV) and 72 mV dec⁻¹ ($\eta = 65\text{-}115$ mV), respectively. These values suggest that the HERs of the as-prepared Mo₂C-based samples undergo Volmer-Heyrovsky pathways. ^[31] When we extended the y-axis of the Tafel slopes to zero, the value of the exchange current density (i_0) could be determined by inverse logarithm of the x-intercept value. The 3DHP-Mo₂C, I-Mo₂C/NCNT, and I-Mo₂C/CNT samples have i_0 values of 2.8×10^{-1} , 1.3×10^{-1} , and 7.1×10^{-2} mA cm⁻², respectively (summarized in Table A.4). Among them, the 3DHP-Mo₂C sample has the highest i_0 value, suggesting that the rate of HER is fast when 3DHP-Mo₂C is used as an electrocatalyst.

Figure 5.13 CV measurements at a range from 0.04–0.44 *versus* RHE without faradic processes. A series of CV measurements were performed at various scan rates for (a) 3DHP-Mo₂C, (b) I-Mo₂C/NCNT and (c) I-Mo₂C/CNT samples. (d) Current density difference ($i_a - i_c$ defined at 0.25 V *versus* RHE) against different scan rates for these electrocatalysts.

To understand the influence of electrochemical surface area (ECSA) of the electrocatalysts towards HER activity, we derive the double-layer capacitance (C_{dl}) of each sample from the CV measurements at various scan rates (Figure 5.13a-c). We plotted the change in current density ($i_a - i_c$) against different scan rates (Figure 5.13d) and divided the slope in this plot by two to obtain the C_{dl} value for each sample. The C_{dl} value is directly proportional to the ECSA of the material. The C_{dl} values 3DHP-Mo₂C, I-Mo₂C/NCNT, and I-Mo₂C/CNT are 21, 12, and 10 mF cm⁻². Among them, the 3DHP-Mo₂C sample has the highest C_{dl} value, implying that it has the highest ECSA. Electrocatalyst with high ECSA means that it has more active sites for HER. As a result, it should exhibit a better HER performances as compared to the material with low ECSA value. These results are in accordance with the HER performances in Figure 5.12a-b. It is notable that Mo₂C embedded in N-doped carbon material (*e.g.* I-Mo₂C/NCNT) has a better HER activity as compared to Mo₂C supported on undoped carbon

(e.g. I-Mo₂C/CNT). We believe that by doping N into CNT, the H-catalyst adsorption strength of the I-Mo₂C/NCNT catalyst is optimized for efficient HER.

Figure 5.14 TOF of the electrocatalysts are derived from (a) SSA (based on BET model) is named TOF_{BET} (see details in Calculation A.3) and (b) RF is named as TOF_{RF} (see details in Calculation A.4).

Figure 5.14a and 5.14b present the turnover frequency (TOF) of the samples derived from BET specific surface area (SSA) and roughness factor (RF) of the material, respectively. At a specified overpotential (η), the TOF is described as the amount of H₂ molecules produced in one second.^[32] The TOF values in this study are summarized in Table A.4. At $\eta = 100$ mV, the microporous 3DHP-Mo₂C has an average TOF of 4.5×10^{-2} H₂ s⁻¹, which is 1.4 times higher than mesoporous I-Mo₂C/NCNT (3.2×10^{-2} H₂ s⁻¹). This result implies that the microporous 3DHP-Mo₂C can produce high capacity of H₂ fuel in one second as a comparison with mesoporous I-Mo₂C/NCNT sample. Meanwhile, the average time to produce one H₂ molecule on the catalyst surface is defined as the reciprocal of the TOF value. The average times for producing one molecule of H₂ at the surface of microporous 3DHP-Mo₂C and mesoporous I-Mo₂C/NCNT are ~ 22 s and ~ 31 s, respectively. This result implies that the former takes a shorter time to generate one H₂ molecule and it has a faster rate of mass transport as compared to the latter material. We believe that this could a possible reason

for the superior HER performances of 3DHP-Mo₂C being obtained in Figure 5.12a-b.

Figure 5.15 (a) Nyquist plots collected on 3DHP-Mo₂C at various overpotentials. (b) Nyquist plots of the I-Mo₂C/CNT, I-Mo₂C/NCNT and 3DHP-Mo₂C recorded at $\eta = 200$ mV in 0.5 M H₂SO₄ solution with inset of Randles circuit model (R_s represents series resistance consists of resistance in wiring, resistance of electrode and solution resistance; R_{ct} symbolizes the charge transfer resistance; C_{dl} denoted as double-layer capacitance).

We further evaluated the HER kinetics of porous Mo₂C sample in the 0.5 M H₂SO₄ solution using an EIS technique to obtain the Nyquist plot (Figure 5.15a-b). The Nyquist plot of 3DHP-Mo₂C was first conducted at various overpotentials of 10, 100, and 200 mV (Figure 5.15a). Then we select the optimized overpotential at 200 mV to evaluate the impedances of the I-Mo₂C/NCNT and I-Mo₂C/CNT samples, as shown in Figure (Figure 5.15b). The Randles circuit model (inset, Figure 5.15b) illustrates the electronic circuit of the electrochemical systems consisting of microporous 3DHP-Mo₂C and mesoporous Mo₂C (*e.g.* I-Mo₂C/NCNT and I-Mo₂C/CNT). At $\eta = 200$ mV, the microporous 3DHP-Mo₂C has a charge transfers resistance (R_{ct}) of ~ 22 ohm, which is lower than that of mesoporous Mo₂C: I-Mo₂C/NCNT (~ 97 ohm) and I-Mo₂C/CNT (~ 105 ohm). We believe that this low R_{ct} value of 3DHP-Mo₂C sample is attributed to the close contact between the Mo₂C and the porous carbon, which facilitates facile electron transport for HER.

Figure 5.16 Durability test of hierarchical 3DHP-Mo₂C consists of polarization curves at 2 mV s⁻¹ and time-dependant current density curve under $\eta = 100$ mV for 28 h in (a-b) pH 0, (c-d) pH 7 and (e-f) pH 14 media.

Figure 5.17 TEM images and SAED patterns of 3DHP-Mo₂C electrocatalyst after being HER electrocatalyzed for 28 h in (a-d) pH 0, (e-h) pH 7 and (i-l) pH 14 solutions.

Figure 5.18 Faraday efficiency of hydrogen generation over 3DHP-Mo₂C at 25 mA cm⁻² measured for 240 min at (a-b) pH 0, (c-d) pH 7 and (e-f) pH 14 media. See details in Calculation A.5.

The durability of the 3DHP-Mo₂C sample was evaluated in various pH solutions of 0, 7, and 14 (Figure 5.16a-f). After 1000 cycles, these graphs show that there is small decay of current densities in pH 0, 7 and 14 media, which indicates that the 3DHP-Mo₂C sample is relatively electrochemical stable in acidic, neutral and basic conditions. Figure 5.17a-l shows that the morphologies and degree of crystallinity of the 3DHP-Mo₂C sample remain unchanged after prolonged cycling for 28 h. This result further verifies that the 3DHP-Mo₂C sample also has a good structural stability in wide range of pH conditions. Lastly, the Faradaic efficiencies of 3DHP-Mo₂C in the three media has excellent stability of ~100% (Figure 5.18a-f).

5.3.3 Proposed HER mechanisms for microporous versus mesoporous Mo₂C electrocatalysts

Figure 5.12c and 5.12d illustrate the proposed mechanisms for HER (microporous Mo₂C versus mesoporous Mo₂C). At an equilibrium state, the reaction ($2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2$) has thermodynamic reduction potential (E° reduction) of 0 V *versus* RHE. Upon the application of voltage (E_{applied}), the HER is driven forward ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$). Nevertheless, due to the slow HER kinetics, the E_{applied} is often deviated from E° reduction. This potential deviation is also described as overpotential (η). It is notable that the effective diameter of H_3O^+ ion is 2.8 Å.^[33] The mesoporous material has a void bigger than microporous material and the former could hold more H_3O^+ ions, as illustrated in Figure 5.12c. Figure 5.12d presents the mass transport pathways of proton in mesopore and micropore. It is known that the proton can be transfer from one end to the other end via the Grotthuss mechanism.^[34] During HER, H_3O^+ ion nearer to the electrode surface get reduced first followed by the reduction of H^+ ion further away from the electrode surface. The H_3O^+ ion that is further away from the electrode surface is denoted as boundary end (marked by a dotted line in Figure 5.12d). The H_3O^+ ion in the micropore takes a shorter pathway to reach the surface for interior core for HER as it has a short boundary end (SBE). On the other hand, the H_3O^+ ion in

the mesopore takes a longer pathway to reach the surface of interior core for HER as it has a long boundary end (LBE). SBE facilitates rapid proton mass transport, leading to the enhancement HER kinetics and thus reduces the diffusion overpotential.

5.4 Conclusion

In summary, for the first time, we have used Na and pyridine mixture to fabricate PNDCF via solvothermal treatment. This as-synthesized PNDCF gives a large SSA of 2330 m² g⁻¹. Next, we fabricated 3DHP-Mo₂C using template-assisted approach by carburizing of Mo-PNDCF hybrid under H₂/Ar condition. The as-obtained 3DHP-Mo₂C sample has a low operating overpotential of 97 mV at 10 mA cm⁻² and a high exchange current density of 2.8×10^{-1} mA cm⁻². The 3DHP-Mo₂C sample with dominant micropores possesses much higher HER activity in comparison with the mesoporous sample (*e.g.* I-Mo₂C/NCNT and I-Mo₂C/CNT). The excellent HER performance of microporous 3DHP-Mo₂C over mesoporous Mo₂C was proposed to be caused by the small pore size effect. As small pore size material could provide a shorter proton mass transport pathway for rapid mass transport of H₃O⁺ ion to the surface of the interior pore for HER. We believe that this unique structure of 3DHP-Mo₂C could be utilized for a broad range of applications involving electrochemical reactions.

5.5 References

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Chapter 6

Tuning the Electronic Structure of Nitrogen/Sulfur Co-Doped Mo₂C Nanosheets for Hydrogen Production

The fabrication of sulfur (S) and nitrogen (N) co-doped Mo₂C nanosheets with thickness of 1.0 nm and facets exposure of (101) through a two-step process was divulged in this study. The synthesis of the layered N/S-doped Mo₂C nanosheets were formulated by the solvent exfoliation of the layered Mo₂C into single nanosheets after the carburization of layered molybdenum oxide/phenol/thioacetamide hybrid. The wetting of the Mo₂C in aqueous electrolyte was caused by the co-doping of N and S. Also, the co-doped N and S heteroatoms enhanced the binding strength of the Mo center towards the hydronium cation (H₃O⁺) and facilitated the generation of H₂ molecules through the cleavage of H-O bond of H₃O⁺ cation. Therefore, a synergistic reactivity towards the hydrogen evolution reaction (HER) was created. Thus, we were able to accomplish a preferable HER performance with a low operating potential of -61 mV at 2 mA cm⁻², which was approximately four orders of magnitude lower than the layered Mo₂C flakes.

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6.1 Introduction

Hydrogen is extensively recognized as a carbon-free fuel and therefore, hydrogen generation via water splitting have been intrigued more attention recently. To manufacture substantial hydrogen, an efficient, economical and sufficient catalyst is needed for the hydrogen evolution reactions (HER). However, the expensiveness and scarcity of the noble metals like platinum (Pt) obstruct their practicality to be employed as the most promising HER catalysts.^[1-3] Hence, scientists are striving to discover the feasibilities of fabrication with numerous noble-metal free catalysts for HER.^[4-8] Due to the excellent electrical conductivity, catalytic activity and chemical stability, molybdenum carbide (Mo₂C or MoC) draws the greatest attention for electrocatalysis among all the proposed noble-metal free catalysts.^[9-11] According to Liao *et al.*, it has been recently revealed that rational design of nanostructures was able to enhance the electrocatalytic properties of Mo₂C further, for instance, the porous molybdenum carbide (Mo₂C) nanowires demonstrated a better HER activity as compared to bulk Mo₂C.^[12] In the past few years, the usage of the 2D nanomaterials in catalysis is emphasized extensively due to their unprecedented electronic properties, superior specific area and particularly, the ease of their surface chemistry manipulation in comparison with the bulk materials.^[13-17] The scrutinization for the preparation of 2D Mo₂C nanostructures and the HER properties are not complete yet in spite of the previous examinations and researches. Additionally, chemical doping is very important for the tuning of materials' surface properties in the aspects of synergistic coupling effect, electronic band structure and wettability properties.^[8, 18-20] With these characteristic modifications, the HER electrocatalytic activities could further be improved. Taking the pure graphene as an example, it exhibits a notably positive Gibbs free energy of hydrogen absorption, $|\Delta G_{H^*}|$, which signifies a low electrocatalytic activity for HER. Nevertheless, $|\Delta G_{H^*}|$ approximates nearly zero when nitrogen/sulfur is chemically doped into the graphene, which indicates a HER activity improvement with the most

advantageous electronic properties.^[21] Furthermore, the wettability of the solid-state surface towards water could be altered by the doping of heteroatom into nanostructure, such as the nitrogen-doped carbon.^[20] The tailored wetting behaviour is able to escalate the electrolyte-electrode contact points, produce a prominent electron transfer by reducing the charge transfer resistance and therefore results in an electrocatalytic activity improvement. Till date, there is no concrete substantiation on the correlation of HER and the wetting behaviour of the Mo₂C nanomaterial yet. The merger of the two previously mentioned strategies, which are the 2D material fabrication and the element doping would be a desirable method to further enhance HER activities.

The synthesis of nitrogen/sulfur co-doped molybdenum carbide (N/S-doped Mo₂C) nanosheets (NSs) is conducted via the carburization of the molybdenum oxide/phenol/thioacetamide hybrid and the subsequent solvent exfoliation of the layered Mo₂C. The dimension of the synthesized products is measured to be 1.0nm thick with a huge SSA of 139 m² g⁻¹. Additionally, we integrated the N and S dopants into Mo₂C and observed a substantial improvement of its wettability, which promoted the process of ion diffusion and expedited the performance rate of HER. Therefore, we propose that the exceptional rate of HER is correlated to the synergistic effect, *e.g.* σ -donation/ π -back donation. This synergistic effect is caused by the N and S doping in the metal complex, which stimulate the dual-functionality of the metal centre, improve the catalyst-H₃O⁺ interaction and diminish the strength of the H-O bond in the hydronium cation (H₃O⁺) to promote the generation of hydrogen molecules. In addition, we have performed density functional theory (DFT) calculation to verify the experimental HER trends: Mo₂C < N-doped Mo₂C < S-doped Mo₂C < N/S-doped Mo₂C. And it seems like our DFT results are in accordance with the experimental results. The synthesized N/S-doped Mo₂C catalyst demonstrated a significantly smaller HER potential of -86 mV at 10 mA cm⁻² with a greater exchange current density of 3.5 x 10⁻² mA cm⁻² as compared to the existing Mo₂C materials illustrated in the previous literatures (see Table A.5).

6.2 Experimental methods

6.2.1 Chemicals and materials

Sodium molybdate dihydrate (Na₂MoO₄·2H₂O, 99%, Sigma-Aldrich), phenol (C₆H₅OH, 99%, Sigma-Aldrich), sodium thiosulfate (Na₂S₂O₃, 99.9%, Sigma-Aldrich), phenylamine (C₆H₅NH₂, 99%, Sigma-Aldrich), thioacetamide (CH₃CSNH₂, 99%, Sigma-Aldrich), formamide (HCONH₂, 98%, Sigma-Aldrich), Nafion solution (0.5 wt%, Sigma-Aldrich), commercial Pt on Vulcan XC-72 (Pt/C, 20 wt%, Premetek), ethanol (CH₃CH₂OH, 99.5%, Sigma-Aldrich), and sulfuric acid (H₂SO₄, 99.999%, Sigma-Aldrich).

6.2.2 Synthesis of the layered MoO_x/C/dopant

For the fabrication of MoO_x/C/N/S, MoO_x/C/S, and MoO_x/C/N samples, 2.2 mmol of phenol, 0.109 mmol of Na₂MoO₄·2H₂O and their respective dopants precursors (0.008 mmol of thioacetamide, 0.004 mmol of sodium thiosulfate, and 0.008 mmol of phenylamine) were dissolved in 4 mL of distilled water. This mixture was added into an autoclave and the reaction vessel was heated at 100 °C for 2 h. After the reaction was completed, the as-obtained MoO_x/C/dopant sample was cleaned using distilled water followed by ethanol. Then the solid products were dried in the vacuum oven at 50 °C overnight.

6.2.3 Synthesis of layered undoped/doped Mo₂C

The as-obtained layered MoO_x/C/dopant samples were heated to 700 °C at a ramping rate of 20 °C min⁻¹ and dwell for 15 min under the 5% H₂/95% Ar atmosphere.

6.2.4 Exfoliation of layered Mo₂C sheets

20 mg of the layered doped Mo₂C samples were stirred in 40 mL of formamide for 24 h. Then the dispersion was further treated via sonication for 48 h under ambient conditions. After 48 h of sonication, single layer Mo₂C NSs were separated from bulk layered Mo₂C through centrifugation. Lastly, the final

products were washed with ethanol and then collected for further characterizations.

6.2.5 Materials characterizations

The morphologies and dimensions of the samples were analyzed using transmission electron microscopy (TEM, model JEM-2100F, 200 keV) and atomic force microscopy (AFM, Bruker Multimode 8). The crystal structures of the samples were characterized using thin film X-ray diffraction (XRD, Shimadzu XRD with Cu-K α irradiation, $\lambda = 1.5406 \text{ \AA}$). The elemental compositions of the samples were analyzed using the energy-dispersive X-ray spectroscopy (EDX) mapping. The surface chemistry on the samples were examined by X-ray photoelectron spectroscopy (XPS, SPECS XR50, X-ray source with $h\nu = 1253 \text{ eV}$ and 200 W). The elemental contents in the samples were determined using Carbon Hydrogen Nitrogen Sulfur (CHNS) elemental analyzer (Elementar Vario Micro Cube) in combine with inductively coupled plasma–optical emission spectrometer (ICP-OES, Dual-view Optima 5300 DV). The SSAs of the samples were characterized by nitrogen adsorption/desorption isotherms using ASAP Tri-star II 3020 model instrument. The contact angles of the samples were measured using DataPhysics (OCA 30) Instrument.

6.2.6 Electrochemical measurements

For the preparation of slurry for HER testing, 5 mg of sample was mixed in 0.9 mL ethanol, 0.1 mL H₂O and 10 μL Nafion. Then the slurry was sonicated for 30 min followed by drop casted 5 μL of the slurry onto the glassy carbon electrode with $\sim 0.07 \text{ cm}^2$ in area, and then dried the prepared working electrode (W.E) at ambient conditions. Linear sweep voltammetry (LSV) was performed at a scan rate of 2 mV s^{-1} in 0.5 M H₂SO₄ using a saturated calaromel electrode (SCE) as the reference electrode (RE) and Pt wire as the counter electrode (CE). All the data were calibrated to reversible hydrogen electrode (RHE) and compensated

for ohmic losses. Electrochemical impedance spectroscopy (EIS) was conducted at different potentials at a frequency window of 0.1 – 10⁵ Hz.

6.3 Principle outcomes

6.3.1 Synthesis and characterizations of N and S doped Mo₂C

Figure 6.1 Schematic illustration of the growth processes of chemically doped Mo₂C NSs.

Figure 6.1 illustrates the growth mechanisms of Mo₂C NSs. In the first step, the Mo precursor, phenol (act as carbon source) and dopants (see Table A.6 for the various types of dopants) were mixed in the autoclave followed by hydrothermal treatment at 100 °C. In the subsequent step, the MoO_x/phenol/dopants composite underwent carbruization process at 700 °C under H₂/Ar (5%/95%) atmosphere to obtain the layered doped Mo₂C. In the last step, the layered doped Mo₂C was mixed with the formamide solvent for exfoliation process. At this stage, the formamide molecules were infused into the spaces of the interlayers, which depressed the van der Waals attractions between the adjacent layers and widened the interlayers length. With the assistance of sonication treatment, these layers

could be separated by the mechanical force and single layer sheets could be obtained.

Figure 6.2 (a) XRD patterns, (b) XPS Mo 3p and N 1s spectrum, and (c) XPS S 2p spectrum of Mo₂C and N/S-doped Mo₂C samples. (d-e) Low-magnified TEM images of Mo₂C and N/S-doped Mo₂C nanosheets, respectively. High magnified TEM images with inset SAED pattern of (f) Mo₂C and (g) N/S-doped Mo₂C. AFM images with inset height profile of (h) Mo₂C and (i) N/S-doped Mo₂C samples.

Figure 6.3 (a) XRD patterns, (b) XPS Mo 3p and N 1s spectrum, and (c) XPS S 2p spectrum of S-doped Mo₂C and N-doped Mo₂C samples. Low-magnified TEM images of (d) S-doped Mo₂C and (e) N-doped Mo₂C samples. High magnified TEM images with inset SAED pattern of (f) S-doped Mo₂C and (g) N-doped Mo₂C. AFM images with inset height profile of (h) S-doped Mo₂C and (i) N-doped Mo₂C samples.

Figure 6.2a and 6.3a show the XRD patterns for N/S-doped Mo₂C, pure Mo₂C, S-doped Mo₂C and N-doped Mo₂C samples, respectively. All the samples have the diffraction peaks of 34.3, 37.7, 39.3, 51.9, 61.5, 69.1, 72.4, and 74.5°, which are corresponding to β -Mo₂C (JCPDS 35-0787). Moreover, the XPS spectrum (Figure 6.2b) of the N/S-doped Mo₂C sample has binding energies of 416.3 eV/397.7 eV (N 1s) and 412.8 eV/394.7 eV (Mo 3p_{1/2}/3p_{3/2}), which are corresponding to the Mo-N bond in the N-doped Mo composite.^[22] In addition, these signals could also be observed in the XPS spectrum of N-doped Mo₂C sample (Figure 6.3b). In addition, the XPS S 2p spectrum (Figure 6.2c) of the N/S-doped Mo₂C sample has binding energies of 163.6 and 162.4 eV, which are

attributed the Mo-S bond in the S-doped Mo composite.^[23] Similarly, these two signals could also be found on the XPS S 2p spectrum of the S-doped Mo₂C (Figure 6.3c). These results indicate that we have successfully doped N and S into the Mo₂C lattice.

Following on, the CHNS-elemental analyzer was further used to quantify the N and S contents in the Mo₂C samples (summarized in Table A.7). It was being estimated that the total amount of N and S level in each sample was about 5 mol%. It is also notable that in combine with ICP-OES measurement, the Mo₂C samples has a molar ratio of Mo/C equals to 2:1. These results reveal that N and S dopants are present in the Mo₂C samples.

Figure 6.4 (a) Large-area AFM image and (b) low-magnification TEM image of N/S-doped Mo₂C nanosheets

The TEM images (Figure 6.2d-e and 6.3d-e) of the Mo₂C NSs samples show that the side-by-side lengths of the sheets are ranging from 0.5 to 1.2 μm. These dimensions could be confirmed by the AFM and TEM analyses in Figure 6.4a-b. The high-resolution (HR) TEM images of (Figure 6.2f-g and 6.3f-g) Mo₂C-based samples reveal that these nanosheets have d-spacings of 0.26 and 0.23 nm, which are attributed to the (010) and (111) atomic planes of the β-Mo₂C, respectively. The spots-like patterns in the SAED images (Figure 6.2f-g, inset and 6.3f-g, inset) indicates that the as-prepared single-layer nanosheets are single crystalline. Also,

these diffraction patterns can be assigned to [101] zone axis, which are reflected by the dominant peak in the XRD pattern. The exposure (101) atomic plane of the Mo₂C crystal structure is being simulated in Figure A.1. The thickness of these single-layer sheets were further confirmed by AFM measurements to be ~ 1.0 to 1.2 nm (Figure 6.2h-i and 6.3h-i).

Figure 6.5 Nitrogen adsorption/desorption isotherms of Mo₂C nanosheets samples. (a) Mo₂C, (b) S-doped Mo₂C, (c) N-doped Mo₂C and (d) N/S-doped Mo₂C.

The SSAs of the doped Mo₂C samples were examined using N₂ adsorption/desorption isothermal analysis. Figure 6.5 reveals that the N/S-doped Mo₂C S-doped Mo₂C, N-doped Mo₂C, and pure Mo₂C NSs samples have SSA of 139, 122, 153, and 124 m² g⁻¹ respectively. The HAADF images and EDX mapping images (Figure 6.6a-m) of these Mo₂C samples reveal that the elements (*e.g.* Mo, C, S, and N) are evenly distributed on the materials.

Figure 6.6 HAADF images and their corresponding EDX mapping images of (a-d) S-doped Mo₂C, (e-h) N-doped Mo₂C and (i-m) N/S-doped Mo₂C samples.

Figure 6.7 Contact angle of the Mo₂C and N/S-doped Mo₂C samples was taken a various time.

Figure 6.8 Contact angle of the S-doped Mo₂C and N-doped Mo₂C samples was taken a various time.

We also investigate the doping effect towards the wetting ability of H₂O on samples surface. Figure 6.7 shows the contact angle of H₂O droplet on N/S-doped Mo₂C sample gradually spread out from the initial contact angle of 25.1° to complete wetting after 10 s, indicating that the N/S-doped Mo₂C sample is hydrophilic. On the other hand, the pure Mo₂C sample has a contact angle of 40.2° (at 0 s) and 18.0° (≥ 10 s). The contact angle of H₂O droplet on pure Mo₂C material is higher than the N/S-doped Mo₂C material, suggesting that the latter is more hydrophilic as compared to the former. Figure 6.8 displays that the S-doped Mo₂C and N-doped Mo₂C materials have contact angles of 8.9 (≥ 10 s) and 9.6° (≥ 10 s), respectively. These results suggest that by co-doping of N and S into Mo₂C, we could enhance the wetting property of the material significantly, which improves the electrode-electrolyte contact points that promote the charge-transfer process during the HER. The wetting property of N/S-doped Mo₂C is better than single doped ones might be because the former has a lower surface energy or more dangling bond on the surface of doped-Mo₂C as compared to the latter.

6.3.2 Comparison of the HER performances of N and S doped Mo₂C

Figure 6.9 LSV curves for layered bulk Mo₂C and Mo₂C samples in 0.5 M H₂SO₄ at 2 mV s⁻¹.

Figure 6.10 (a) LSV curves, (b) Tafel plots, (c-d) durability test of Mo₂C, S-doped Mo₂C, N-doped Mo₂C, N, S-doped Mo₂C and Pt/C samples in 0.5 M H₂SO₄ at 2 mV s⁻¹. The TEM image and SAED pattern of N/S-doped Mo₂C sample after stability test.

The HER performances of the electrocatalysts were examined in 0.5 M H₂SO₄ solution using a three-electrode system. For comparison reason, commercial Pt/C (20 wt%) and bulk layered Mo₂C were also evaluated. It is notable that the onset potential of ultra-thin Mo₂C NSs (234 mV), which is noticeably lower than that of bulk Mo₂C (249 mV), as depicted in Figure 6.9. We believe that the remarkable HER activity of the Mo₂C NSs over the bulk Mo₂C is due to the advantageous electronic band of the single-layer sheet material. The LSV curve (Figure 6.10a) and Tafel slope (Figure 6.10b) of the Pt/C electrode shows an excellent HER activity consisting of onset potential (close to 0 mV) and a Tafel slope of 30 mV dec⁻¹. The doped Mo₂C NSs electrodes of N/S-doped Mo₂C NSs, S-doped Mo₂C NSs, and N-doped Mo₂C NSs have onset potentials of 46, 144, and 186 mV. Among them, the N/S-doped Mo₂C sample has the lowest onset

potential, which indicates that it is an efficient HER catalyst. Figure 6.10b presents a Tafel graph plotted voltage along the y-axis against the logarithm current of density along the x-axis. The slope on this graph is known as the Tafel slope and the values of this slope determine the rate-limiting step of the reaction pathways for HER.^[24] These reaction pathways were mentioned earlier in Chapter 5 (see section 5.3.2). The N/S-doped Mo₂C NSs, S-doped Mo₂C NSs, N-doped Mo₂C NSs, and Mo₂C NSs electrodes have the Tafel slopes of 47 mV dec⁻¹ ($\eta = 59$ -101 mV), 60 mV dec⁻¹ ($\eta = 176$ -232 mV), 63 mV dec⁻¹ ($\eta = 211$ -265 mV), and 75 mV dec⁻¹ ($\eta = 240$ -331 mV), respectively. These Tafel slope values suggest that the HERs of the above materials undergo a Volmer-Heyrovsky mechanism where the Volmer reaction is the rate-determining step.^[25] Among them, N/S-doped Mo₂C NSs electrode has the lowest Tafel slope value, indicating that it has the fastest HER kinetics.

The electrochemical stability of N/S-doped Mo₂C NSs was evaluated in 0.5 M H₂SO₄ electrolyte (Figure 6.10c). After sweeping for 1000 cycles, the N/S-doped Mo₂C NSs sample displays a slight decay of overpotential by 1 mV at 10 mA cm⁻². In addition, upon the application of constant potential of 100 mV on the N/S-doped Mo₂C NSs electrode for 28 h, only slight drop of current density of 2 mA cm⁻² is being observed (Figure 6.10d). In the inset of Figure 6.10d, the morphology and crystallinity of the N/S-doped Mo₂C NSs remain unchanged after long-cycling for 28 h, which suggest that N/S-doped Mo₂C NSs material has an excellent structural stability.

The exchange current densities of N/S-doped Mo₂C NSs, S-doped Mo₂C NSs, N-doped Mo₂C NSs, and undoped Mo₂C NSs electrodes are 3.8×10^{-2} , 3.9×10^{-3} , 1.2×10^{-3} , and 7.9×10^{-4} mA cm⁻², respectively (summarized in Table A.8). Among them, the N/S-doped Mo₂C NSs electrode has the highest exchange current density value, which implies that less energy is required to drive large current flow. In addition, the N/S-doped Mo₂C NSs electrode exhibits a low

operating potential of 86 mV at current densities of 10 mA cm⁻¹, which is the best that has ever reported (compare with other literature values in Table A.5).

Figure 6.11 EIS analysis of fitted (a) Nyquist plot of N/S-doped Mo₂C sample in 0.5 M H₂SO₄ at various overpotentials and (b) EIS of Mo₂C samples at 200 mV in 0.5 M H₂SO₄ solution.

Furthermore, we evaluated the HER activity of the doped Mo₂C NSs sample in the 0.5 M H₂SO₄ solution using an EIS technique. The Nyquist plot of N/S-doped Mo₂C sample was first performed at various overpotentials of 10, 100, and 200 mV (Figure 6.11a). Then we select the optimized overpotential at 200 mV to investigate the impedances of the doped Mo₂C and pure Mo₂C samples, as depicted in Figure 6.11b. The impedance at high frequency is known as the Ohmic resistance (R_s), which is corresponding to the internal resistance of the electrolyte.^[26] Whereas, the impedance at low frequency is referred to the charge transfers resistance (R_{ct}).^[26] The N/S-doped Mo₂C NSs electrode has a smaller R_{ct} as compared to singly doped Mo₂C and pure Mo₂C electrodes. We believe that this small R_{ct} is attributed to the excellent wettability of N/S-doped Mo₂C NSs towards aqueous solution.

6.3.3 Proposed HER mechanisms for N and S doped Mo₂C

Figure 6.12 (a) Proposed catalytic cycle for HER. (b) Synergistic effect of N, S doped Mo₂C. (c) HOMO of S→Mo⁽ⁿ⁾L_n complex π back donation to LUMO of H₃O⁺. The energy levels of the molecular orbitals of H₃O⁺ are taken from reference [27].

Figure 6.12a-b illustrate the proposed mechanism for N and S co-doped Mo₂C. In addition to the common Volmer-Tafel or Volmer-Heyrosky mechanisms, an alternative mechanism related to organometallic chemistry and molecular orbital theories using catalytic cycle for HER is being proposed in this study. Typically, the electrochemical reaction usually occurs at the surface of the catalyst. Along the catalyst surface, there are dangling bonds, which consist of metal complex (MoL_n). During HER in acidic solution, it is often being assumed that the major species in the electrolyte is H₃O⁺ ion. [28] In electrocatalysis, the active sites could also be defined as crystal defects or coordinative unsaturated sites (CUS). [29] Previous study has shown that the (100), (101) and (201) facets of β-Mo₂C phase

have many CUS.^[30] Figure 6.12a presents the catalytic cycle for HER upon the application of negative potential. In step (1), the H₃O⁺ ions form bond with the CUS on the MoL_n complex via association process. In step (2), the oxidation state of MoL_n complex increases by 2 due to the oxidative addition reaction. During oxidative addition, the hydrides are covalently bonded to the Mo centre. In step (3), these hydrides are being converted to H₂ molecule via reductive elimination process. During reductive elimination process, the oxidation state of the metal centre is being reduced back to “n” state. The formation of H₂ molecule form σ -bonding with the metal centre. In addition, this metal centre to H₂ bond is proven to be labile and it can be easily replaced by H₃O⁺ ion,^[31] As a result, the H₂ molecule is being released back into the solution via dissociation process in the step (4).

Previous studies have reported that N heteroatom is an electron acceptor,^[18,32] while S heteroatom is an electron donor.^[18] Based on this knowledges, we proposed a synergistic effect of N/S -doped Mo₂C for HER in Figure 6.12b and c. The N atom in the N←Mo⁽ⁿ⁾L_n complex decreases the basicity of the Mo centre, making the Mo centre to be slightly electropositive (δ^+), which is favourable to form Mo⁽ⁿ⁾L_n-H₃O⁺ complex via σ -bonding. On the other hand, the S atom in the S→Mo⁽ⁿ⁾L_n complex increases the basicity of the Mo centre, which promotes π -back donation to the antibonding orbital (LUMO) of H₃O⁺ state (Figure 6.12c). As a result, in the H-O bond in the H₃O⁺ cation is broken, leading to the formation of H₂ molecule. This electron donor-acceptor pair of S and N induces synergistic effects in the N/S-doped Mo₂C, which leads to the improvement of HER performances. In addition, we have performed DFT calculation to verify the experimental HER trends: Mo₂C < N-doped Mo₂C < S-doped Mo₂C < N/S-doped Mo₂C. And it seems like our DFT results are in accordance with the experimental results. The free energies (ΔG_H^*) of Mo₂C, N-doped Mo₂C, S-doped Mo₂C and N/S-doped Mo₂C are -1.03, -0.93, -0.83 and -0.79 eV, respectively. The $|\Delta G_H^*|$ value is closed to zero, implying that the electrocatalyst is an efficient HER catalyst.

6.4 Conclusion

In conclusion, we have fabricated the Mo₂C NSs with thickness of 1.0-1.2 nm via carburization in combine with solvent exfoliation process. These ultra-thin Mo₂C sheets possess large SSAs (*e.g.* 122-153 m² g⁻¹) and their unique electronic band structure favors efficient HER in comparison with the bulk layered Mo₂C. The HER activity can be further improved by chemically doped N and S into the Mo₂C lattice. The N/S-doped Mo₂C NSs exhibits a low operating potential of 86 mV at a current density of 10 mA cm⁻². We believe that this superior HER performances of dual-doped Mo₂C over singly doped Mo₂C is caused by the synergistic effects and excellent wetting property of N/S-doped Mo₂C NSs electrode towards water splitting reaction. We also envisage that the N/S-doped Mo₂C NSs can be extended to other aqueous electrochemical reactions.

6.5 References

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Chapter 7

Discussion and Future Work

In this chapter, the threads of rational-designed electrocatalysts for achieving high energy efficiency are drawn together. Next, conclusions drawn from our findings and the impacts of our findings for developing an efficient electrocatalysis will be presented. Following on, the outcomes reflected on the hypotheses will be discussed. In the reconnaissance work and future work section, rational-design of electrocatalysts for Li-O₂ battery and hydrogen production applications will be addressed. Lastly, outstanding questions related to the future works will be discussed.

7.1 General Discussion

Currently, the world is relying on fossil fuels as an energy supply. However, unsustainable energy supply and demand have serious implications toward household budget, national economy, and local air pollution.^[1] In the past few years, many studies have shown that energy efficient in the power grids offer opportunities to save cost while reducing carbon footprint.^[2] And, being energy efficient means less energy is used for doing the same work.^[3] In this thesis, we developed several methods/hypotheses to improve the energy efficiency of high energy storage devices (*e.g.* Li-O₂ battery and H₂ fuel) by rational-design of the electrocatalysts. The major challenge of these high energy storage devices that involve electrocatalytic processes is that large overpotential caused by slow reaction kinetics that results in poor energy efficiency. In this dissertation, we have rational designed the electrocatalysts to resolve the above issue and they are categorized into three parts/hypotheses: (1) “wetting” property of Li₂O₂ on metal oxide (MO) for Li-O₂ battery (**Chapter 4**); (2) porous Mo₂C electrocatalysts for efficient hydrogen evolution reaction (HER) in **Chapter 5**; (3) tuning the electronic structure of heteroatoms (*e.g.* N and S) doped Mo₂C for efficient HER (**Chapter 6**). The ultimate goal for this study is to lower the overpotential of the electrochemical reactions so as to achieve a high energy efficient in high energy storage devices. In **Chapter 4**, we improved the “wetting” property of Li₂O₂ on MO (*e.g.* IrO₂ and CuO) to lower the charging voltage in Li-O₂ battery. In **Chapter 5**, we fabricated microporous Mo₂C electrocatalyst for improving the HER kinetics. In **Chapter 6**, we tuned the electronic structure the electrocatatylst by co-doping N and S into Mo₂C lattice to lower the HER operating potential. The details of the outcome reflected on the hypothesis for individual chapter will be discussed in the following three sections (section 7.1.1, 7.1.2, and 7.1.3). We envisage that our work will enlighten new idea to the energy storage committee, which make a great impact on clean energy economy.

7.1.1 Outcome reflected on hypothesis #1

In **Chapter 4**, the hypothesis is to test whether if the Li_2O_2 molecules form during discharging has better “wetting” on MO over noble metal. Our results show that in the presence of MO (*e.g.* CuO or IrO_2) on noble metal (*e.g.* Pt), the MO/Pt batteries tend to form Li_2O_2 thin layer on the electrode surface rather than large spherical Li_2O_2 NPs on the pure Pt electrode surface during the discharging of Li- O_2 battery. In addition, we observe that in the presence of MO, the wetting property of MO/Pt electrode towards H_2O is better than on Pt electrode. Based on our results, it seems like there is a relationship between the affinity of Li_2O_2 -MO interaction (characterized using TEM) and the wetting behavior H_2O -MO interaction (characterized using contact angle measurement). Also, based on these observations, it seems like there is a thread as such: when the wetting property of H_2O -MO improves, the affinity of Li_2O_2 -MO also improves. We proposed that the plausible reason for these Li_2O_2 -MO interaction and H_2O -MO interaction is due to the ionic characteristic of the MO, which is capable of forming electrostatic interaction with Li_2O_2 and hydrogen bonding with H_2O , respectively. Therefore, this “wetting” property of the electrocatalyst was suggested to be the key for improving the electrochemical performances in Li- O_2 battery. By introducing MO (*e.g.* CuO or IrO_2) onto Pt surface, we can manipulate the morphology of Li_2O_2 formation to thin layer structure, which provides a shorter electron transport pathway for oxygen evolution reaction (OER) that accelerates the reaction kinetics and reduces the charging voltage of Li- O_2 battery. For example, Li- O_2 battery with CuO/Pt NWs has a charging voltage of 3.32 V *versus* Li^+/Li , which is lessened than the Li- O_2 battery with Pt NWs (4.20 V *versus* Li^+/Li).

The first hypothesis of introducing MO on the noble metal surface provides better “wetting” ability of Li_2O_2 on the oxygen cathode and it is proven to be true while the objective of designing a MO/Pt system to form Li_2O_2 thin layer that lowers the charging voltage of Li- O_2 battery has also been met.

7.1.2 Outcome reflected on hypothesis #2

In **Chapter 5**, we have proposed that the transition-metal based electrocatalyst (TMBE) with small pore size distribution could facilitate rapid proton diffusion during the HER, leading to lowering of HER operating potential. To test this hypothesis, we have fabricated microporous Mo₂C in comparison with mesoporous Mo₂C. Based on our HER evaluation, the microporous Mo₂C (*e.g.* 3DHP-Mo₂C) and mesoporous Mo₂C (*e.g.* I-Mo₂C/NCNT) samples have an operating overpotentials of 97 and 148 mV at 10 mA cm⁻², respectively. In addition, the SSA of the as-synthesized microporous 3DHP-Mo₂C material is 302 m² g⁻¹, which is larger than that of the mesoporous I-Mo₂C/NCNT sample (*e.g.* 109 m² g⁻¹). The former with a larger SSA contains more reaction sites that can improve the HER kinetics. In addition, the microporous Mo₂C (*e.g.* 3DHP-Mo₂C) has an estimated average turnover frequency (TOF) of 4.5×10^{-2} H₂ s⁻¹ at $\eta = 100$ mV, which is 1.4 times greater than that of mesoporous I-Mo₂C/NCNT (3.2×10^{-2} H₂ s⁻¹ at $\eta = 100$ mV). This result implies that the former generates more H₂ products per unit time as compared to the latter. Based on our results and observations, this microporous electrocatalyst not only possesses large surface area (*e.g.* increases the availability of reaction sites), but also improve the rate of ion diffusion (*e.g.* enhances reaction kinetics). Therefore, the synthesis of electrocatalyst with dominant micropores is very essential for an efficient HER. The second hypothesis of fabricating microporous TMBE improves the HER kinetics and lower the HER overpotential is proven to be accurate while the aim of designing a microporous 3DHP-Mo₂C materials to facilitate fast ion transport that improves the TOF is also achieved.

7.1.3 Outcome reflected on hypothesis #3

In **Chapter 6**, we have proposed that by chemically co-doping, such as N and S into the Mo₂C lattice, the electronic structure of the Mo₂C could tune to facilitate moderate catalyst-adsorbate interaction in HER. This moderate catalyst-adsorbate interaction is very important for any catalytic processes. According to

Sabatier's principle (as described in **Chapter 2**), a good catalyst is capable of binding the adsorbate with a moderate binding strength.^[4] For instance, if the binding strength is too weak, no reaction will occur, whereas, if the binding strength is too strong the adsorbate will block the catalytic site and impede further reaction. In **Chapter 6**, our results show that the N/S co-doped Mo₂C electrode exhibits the lowest onset overpotential as compared to singly doped Mo₂C and pure Mo₂C. For instances, the onset overpotentials of N/S co-doped Mo₂C, S-doped Mo₂C, N-doped Mo₂C, and pure Mo₂C are 46, 144, 186, and 234 mV. Based on our hypothesis, the N heteroatom behaves like an electron acceptor, which diminishes the basicity of the metal center, making the metal center susceptible to form bond with H₃O⁺ cation via σ donation. Meanwhile, the S heteroatom acts as electron donor, which enhances the H₂ production by H-O bond cleavage of H₃O⁺ via π -back donation. This synergistic effect induces a moderate catalyst-adsorbate interaction in the N/S co-doped Mo₂C electrode, which improves the HER activity and enhances the wettability towards aqueous solution for facile charge transfer.

The third hypothesis suggests that by chemically co-doped (for examples: N and S) Mo₂C lattice, we could adjust the binding strength (close to moderate mode) between the TMBE and adsorbate for improved HER activity is proven to be correct. In addition, the goal of fabricating a TMBE with moderate catalyst-adsorbate interaction to lower the onset overpotential of HER is also achieved.

7.2 Reconnaissance work, future work, and outstanding questions

As discussed earlier in section 7.1, studies have demonstrated that the rational design by tuning the “wetting”, pore size, and electronic structure properties of electrocatalysts could accomplish the ultimate goal of lowering the overpotential of electrocatalysis. In the following sections 7.2.1 and 7.2.3, we also discuss the alternative methods that can be used to lower the overpotential in Li-O₂ battery (*e.g.* future work #1: using solar light energy as an additional energy source) and in HER (*e.g.* future work #2: tuning the electronic property of catalyst-H

adsorption by metal doping into the W_2C lattice). In addition, outstanding questions related to future works #1 and #2 will be discussed in sections 7.2.2 and 7.2.4, respectively.

7.2.1 Future work #1: Photocatalytic Li-O₂ battery

Figure 7.1 (a) Schematic illustration of a 3-electrode photocatalytic Li-O₂ battery consists of Li anode, carbon cathode for discharging, and dye-sensitized TiO₂ photoelectrode for charging process. (b) Charging voltage profile of photocatalytic Li-O₂ battery with dye-sensitized TiO₂ electrode. (a-b) Reproduced with permission from^[5]. Copyright © 2014. Nature Publishing Group. (c) Schematic representation of a 2-electrode system consists of Li anode and C₃N₄ grown on carbon paper. (d) Discharging/charging voltage profile of photocatalytic Li-O₂ battery with C₃N₄. (c-d) Reproduced with permission from^[6]. Copyright © 2015. The Royal Society of Chemistry.

Previously, great efforts have been made to minimize the charging voltage of Li-O₂ battery, such as: (1) synthesizing an efficient OER electrocatalysts (*e.g.* Pt, Co₃O₄, and RuO₂) to effectively diminish the charging voltage (*e.g.* ≥ 3.5 V);^[7-9] (2) using a redox mediator (*e.g.* I⁻/I₃⁻) could further reduced the charging voltage to ~ 3.25 V.^[10] Nevertheless, reports on the lowering of charging voltage below 2.96 V are relatively rare.

Recent studies have shown that by using solar energy, we could achieve a charging voltage below the thermodynamic potential of Li_2O_2 (e.g. 2.96 V). For instance, Wu *et al.* have configured a solar Li- O_2 battery, which composes of three-electrode system. The setup of this solar Li- O_2 battery consists of a Li foil, carbon-based cathode and photoelectrode made of dye-sensitized TiO_2 . The charging voltage of this solar Li- O_2 battery can be reduced to 2.7 V, which is surprisingly below the thermodynamic potential of Li_2O_2 (Figure 7.1a-b).^[5] Inspired by this finding, Zhou *et al.* incorporate photoactive material (e.g. C_3N_4 grown on carbon paper) to serve as the photoelectrode (Figure 7.1c).^[6] Their results show that by illuminating the Li- O_2 battery containing the C_3N_4 grown on carbon paper during the charging process, the charging voltage can be lowered to 1.9 V (with light), as shown in Figure 7.1d. For the future work, we proposed that semiconductor metal oxide (MO) coated with a suitable organic photovoltage (OPV) material can be used for this photocatalytic effect study. However, MOs are relatively low in electrical conductivity, therefore, mixing the MO@OPV material with electrical conducting carbon (e.g. SuperP) may improve the ORR kinetics during discharging, and thus increase the discharge capacity. The selection of OPV material requires several band alignment criteria and it will be discussed in the following section 7.2.2.

7.2.2 Outstanding question for future work #1: How can we lower the charging voltage of Li- O_2 battery using solar light?

Figure 7.2 (a) Schematic representation of the proposed mechanism for photocatalytic charging process in the photocatalytic Li-O₂ battery with dye-sensitized TiO₂ photoelectrode. (a) Reproduced with permission from^[5]. Copyright © 2014. Nature Publishing Group. (b) Schematic illustration of the proposed mechanism for photocatalytic charging process in the photocatalytic Li-O₂ battery with C₃N₄ photoelectrode. (b) Reproduced with permission from^[6]. Copyright © 2015. The Royal Society of Chemistry.

Figure 7.2a-b illustrate the band alignment conditions of the materials needed for photocatalytic charging. Based on the proposed mechanism in Figure 7.2a-b, a suitable photoactive materials (*e.g.* N719 dye or C₃N₄) need to meet the following requirements: (1) the lower energy level (*e.g.* HOMO or VB) of the photoactive materials should be lower than the energy level of the I⁻/I₃⁻ redox couple (denoted as M^{ox}/M^{red} in Figure 7.2a) for the oxidization of 3I⁻ → I₃⁻ + 2e⁻; (2) the higher energy level (*e.g.* LUMO or CB) of the photoactive material should be below the energy level of Li reference (see Figure 7.2b) for enabling the photocatalytic charging effect in Li-O₂ battery. In general, materials with metallic property is often desirable to be used for electrocatalysis due to its high electrical conductivity. Unfortunately, these metallic materials often cause photo-bleaching of the attached photoactive material, which makes them unsuitable as photocatalytic electrode. Therefore, an alternative material, such as MO semiconductor is being considered. The requirements for selection of MO materials are as such: (1) the CB energy level of MO (*e.g.* TiO₂) should be below than the LUMO energy level of the light-absorbing material (*e.g.* N719 dye) for transferring of charges from LUMO state in N719 dye to CB state in TiO₂, as illustrated in Figure 7.2a; (2) the CB energy level of TiO₂ should be above the LUMO energy level of the N719 dye to prevent the recombination of electron-hole pairs.

For example, the photocatalytic charging process of the Li-O₂ battery can be described in Figure 7.2b. During charging under light radiation, the electrons from the VB of C₃N₄ are excited to its CB followed by transferring to the external

circuit of the Li-O₂ cell, reducing Li⁺ ion to Li metal. Meanwhile, the holes generated at the VB of C₃N₄ oxidizes the I⁻ ion to I₃⁻ ion, and subsequently the I₃⁻ ion oxidizes the Li₂O₂ product to O₂ molecule and Li⁺ ion, converting I₃⁻ ion back to I⁻ ion. The completion of redox cycle generates photovoltage that lowers the applied charging voltage. It is being suggested that the theoretical photocatalytic charging voltage (estimated to be 1.7 V), which is equal to the subtraction of Li potential and the CB of C₃N₄.^[6]

7.2.3 Future work #2: Electrochemical Tuning of M-doped (M: Fe, Co, Ni) W₂C for HER

Figure 7.3 (a) Schematic diagram illustrating the growth processes for M-doped (M: Fe, Co, Ni) W₂C nanosheets arrays (NSAs) on tungsten (W) substrate. (b) LSV curve of W substrate and (c) LSV profiles of the Pt/C, W₂C, Fe-doped W₂C, Co-doped W₂C, and Ni-doped W₂C NSAs at 2 mV s⁻¹ in 0.5 M H₂SO₄ (pH 0) solution.

Figure 7.3a shows the growth mechanisms of M-doped (M: Fe, Co, Ni) W₂C NSAs on W substrate. Step 1: growth of WO₃ NSAs on the W substrate via hydrothermal treatment. Step 2: growth of WO₃/G/M hybrid (G: glucose) on the pre-synthesized WO₃ NSAs through hydrothermal carbonization. Step 3: formation of M-doped W₂C NSAs by carburization of the WO₃/G/M hybrid NSAs for HER.

Next, we evaluate the HER performances of M-doped W_2C electrodes in 0.5 M H_2SO_4 solution by scanning the potential at a rate of 2 mV s^{-1} (Figure 7.3b-c). For comparison reason, the W substrate, pure W_2C NSAs, and the Pt/C were also studied. It is notable that the W substrate shows little HER activity (Figure 7.3b). While, the W_2C NSAs electrode exhibits lower onset potential as compared to W substrate. In addition, this onset potential could be further lessened by chemically doped metal (M: Fe, Co, Ni) into W_2C lattice. For instance, Ni-doped W_2C , Co-doped W_2C , Fe-doped W_2C , and pure W_2C NSAs electrodes display onset overpotentials of 4, 45, 78, and 122 mV, respectively (Figure 7.3c). Among them, the Ni-doped W_2C NSAs electrode exhibits the lowest onset potential, suggesting that it is an efficient HER electrocatalyst. In the future work, we suggested that the Ni-doped W_2C material can be evaluated in the sea water for more realistic implementation.

7.2.4 Outstanding question for future work #2: How do we improve the HER activity by doping (M: Fe, Co, Ni) into W_2C lattice?

Figure 7.4 (a) The calculated free energy (ΔG_{H^*}) diagram of the M-doped W_2C surface (M: Fe, Co, Ni) and pure W_2C models for HER at equilibrium potential ($U_{RHE} = 0 \text{ V}$). (b) Volcano plots of i_o in logarithm scale versus free ΔG_{H^*} values of electrocatalysts reported in the literature and in this work (data collected from references is summarized in Table A.9).

To find out the influences of different metal dopants (M: Fe, Co, and Ni) in W_2C

toward HER activity, we conducted organized tests on the electronic properties of pure W_2C and M-doped W_2C (M: Fe, Co, and Ni) models by using density functional theory (DFT) computations. The overall HER mechanism is divided into three stages: (Stage 1) reactant species (*e.g.* $H^+ + e^-$); (Stage 2) intermediate species (*e.g.* catalyst-H, denoted as H^*); (Stage 3) product species (*e.g.* $1/2 H_2$).^[11-12] When the $|\Delta G_{H^*}|$ value is closed to zero, the HER activity is considered to be the most effective. Moreover, when the ΔG_{H^*} value is negative means that the H^* adsorption is strong. Meanwhile, if the ΔG_{H^*} value is positive implies that the H^* adsorption is weak (as discussed in **Chapter 2**).^[12] Among the W_2C -based models in Figure 7.4a, pure W_2C has the most negative ΔG_{H^*} value (-0.27 eV), implying that the HER activity is poor. After incorporating Fe, Co, and Ni dopants into the W_2C , the ΔG_{H^*} values could be changed to -0.16 , -0.05 , and -0.04 eV, respectively. The Ni-doped W_2C model exhibits the lowest $|\Delta G_{H^*}|$ value, representing that it has the highest HER activity with an optimal H^* adsorption strength.

Figure 7.4b displays a typical volcano plot. It is plotted in term of the measured exchange current density (i_0) against the computed Gibbs free energy of H^* absorption (ΔG_{H^*}). This volcano plot is often use as benchmark to compare the HER activity of our electrocatalyst to that of the others reported in the literature. By collecting the i_0 data and ΔG_{H^*} data from the HER tests and DFT computation, respectively, we could designate a point (expresses the HER activity) on the volcano-shaped graph. The point closer to the volcano peak implies that the catalysts could carry out the HER more efficiently. Based on both the i_0 and the ΔG_{H^*} values of the Ni-doped W_2C in Figure 7.4b, we can conclude that the Ni-doped W_2C has a superior HER activity that outperform the other electrocatalysts and it has a comparable activity towards noble metals (*e.g.* Pt and Pd). These results suggest that we could improve the HER activity by tuning the electronic band of the electrocatalyst using chemically doping strategies.

7.3 References

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Appendix

Appendix 1: Supplementary information for Chapter 4

Table A.1 The total specific capacity of Li-O₂ batteries with electrodes (*e.g.* Pt NSs and CuO/Pt NSs) during the 1st full discharge at various current density. ^aMeasured specific capacity taken from Figure 4.17a and b. ^bTotal specific capacity calculated based on Calculation A.1.

Cathode	Current density [mA g ⁻¹]	Total discharged capacity Q [C]	$q_{measured}^a$ [mAh g _{electrode} ⁻¹]	$q_{electrode+Li_2O_2}^b$ [mAh g _{electrode+Li_2O_2} ⁻¹]
Pt NSs	100	5.93	1648	683
	500	3.78	1050	553
	1000	2.20	612	401
CuO/NSs	100	4.53	1259	606
	500	2.78	773	465
	1000	1.61	448	324

Calculation A.1: Determination of total specific capacities

From the measured specific capacities, the total specific capacities of cathode including mass of Li₂O₂ and electrode are calculated using

$$\text{Faraday's laws: } m_{Li_2O_2}(g) = \frac{Q}{F} \times \frac{M}{z}$$

where

1. m is the mass of Li₂O₂ (mass of electrode: $m_{electrode} = 1.00$ mg)
2. Q is the total discharged capacity (C) = $q_{measured}(C) \times m_{electrode}(g)$
[unit conversion: 1 mAh = 3.6 C]

$$3. \quad q_{\text{electrode}+\text{Li}_2\text{O}_2} (\text{mAh g}_{\text{electrode}+\text{Li}_2\text{O}_2}^{-1}) = \frac{q_{\text{measured}}}{m_{\text{electrode}} + m_{\text{Li}_2\text{O}_2}}$$

where Q (C), $m_{\text{electrode}}$ (g) and $m_{\text{Li}_2\text{O}_2}$ (g). Unit conversion: 1 mAh=3.6C.

4. F is the Faraday constant (96485 C mol⁻¹)
5. M is the molar mass of Li₂O₂ ($M= 45.882$ g mol⁻¹)
6. z is the number of electron by assuming final product is Li₂O₂ ($z=2$)

Appendix 2: Supplementary information for Chapter 5

Table A.2 Operating HER overpotential of different Mo-related materials reported previously.

Catalyst	η (mV) at $j= 10$ (mA cm ⁻²)	References
1T- MoS ₂ nanosheets	-210	[1]
MoP particles	-250	[2]
MoB particles	~-215	[3]
Mo ₂ C nanowires	~-200	[4]
Mo ₂ C nanotubes	~-112	[5]
Commercial bulk Mo ₂ C	-310	[6]
Mo ₂ C nanosheets	~-240	[7]
Mo ₂ C/rGO	-130	[8]
Mo ₂ C/N-doped CNT	-147	[9]
Mo ₂ C/multiwalled CNT	-325	[10]
3D Mo _x C/Ni network	-150	[11]
3DHP-Mo ₂ C	-97	This work

Table A.3 Elemental composition of the as-prepared Mo₂C/C_{support} sample derived from ICP-OES elemental analysis and CHNS elemental analyzer.

Sample	Element content (wt%)		
	Mo ₂ C	C _{support}	N
3DHP-Mo ₂ C	29.96	69.39	0.65
Mo ₂ C/NCNT	29.75	69.65	0.60
Mo ₂ C/CNT	30.39	69.61	

Calculation A.2: Determination the Mo₂C loading in Mo₂C/C_{support} sample using ICP-OES and CHNS analyses

The method of determination of Mo₂C loading in Mo₂C/C_{support} sample using ICP-OES elemental analysis is according to literature reported previously.^[12] 5 mg of Mo₂C/C_{support} sample was digested by 1 mL of 65 wt% HNO₃, then diluted to 100 mL volumetric flask.

Let the number of mole of Mo (N_{Mo}) present in the sample be (x) and the calculation is as following,

$$N_{Mo} = x = C_{Mo} \times V_{flask} / M_{Mo}$$

where

- N_{Mo} is the number of mole of Mo in the sample [mol]; defined as “x”
- C_{Mo} is the measured concentration of Mo ions in the solution [mg L⁻¹]; C_{Mo} for 3DHP-Mo₂C, Mo₂C/NCNT and Mo₂C/CNT is 14.1 mg L⁻¹, 14.0 mg L⁻¹ and 14.3 mg L⁻¹, respectively. Convert [mg L⁻¹] to [g L⁻¹].
- V_{flask} is the total volume of the prepared sample solution in the volumetric flask [L]
- M_{Mo} is the molar mass of Mo [95.94 g mol⁻¹]

If “x” is the number of mole of Mo in Mo₂C, then “x/2” is the number of mole of C in Mo₂C.

Therefore, the weight percentage ($wt\%$) of Mo_2C in $\text{Mo}_2\text{C}/\text{C}_{\text{support}}$ sample = $(M_{\text{Mo}_2\text{C}} \times x/2) / m_{\text{total}} \times 100\%$

where

- $M_{\text{Mo}_2\text{C}}$ is the molar mass of Mo_2C [$203.88 \text{ g mol}^{-1}$]
- m_{total} is the mass of total $\text{Mo}_2\text{C}/\text{C}_{\text{support}}$ sample used for digestion [0.005 g]

Since the atomic weights between C and N is quite similar; N content in the material is low (less than $1 \text{ wt}\%$), the contribution of N is negligible in the above calculation.

Table A.4 Comparison of HER performances of the electrocatalysts in $0.5 \text{ M H}_2\text{SO}_4$ with their respective SSAs and dominant PSDs peak width.

Electrocatalyst	Onset potential [mV]	Tafel slope [mV dec ⁻¹]	Exchange current density [mA cm ⁻²]	TOF _{BET} [$\text{H}_2 \text{ s}^{-1}$] at $\eta=100 \text{ mV}$	TOF _{RF} [$\text{H}_2 \text{ s}^{-1}$] at $\eta=100 \text{ mV}$	TOF _{ave} [$\text{H}_2 \text{ s}^{-1}$] at $\eta=100 \text{ mV}$	SSA [$\text{m}^2 \text{ g}^{-1}$] (based on BET model)	Dominant PSD peak widths [$\text{\AA}$] (based on BJH model)
I- $\text{Mo}_2\text{C}/\text{CNT}$	-65	72	7.1×10^{-2}	2.8×10^{-2}	1.1×10^{-2}	2.0×10^{-2}	101	340
I- $\text{Mo}_2\text{C}/\text{NCNT}$	-50	71	1.3×10^{-1}	4.7×10^{-2}	1.7×10^{-2}	3.2×10^{-2}	109	287
3DHP- Mo_2C	-35	60	2.8×10^{-1}	5.8×10^{-2}	3.2×10^{-2}	4.5×10^{-2}	302	11
Pt/C	0	32	8.2×10^{-1}	-	-	-	-	-

Calculation A.3: Determination of TOF_{BET}

The unit cell of Mo_2C contains 3.5 Mo atoms and the surface active sites are assumed to be (100) and Mo atom terminated with a surface area per unit cell of $3.13 \times 10^{-19} \text{ m}^2$.^[13] Therefore, the number of surface Mo sites per m^2 geometric area ($n_{\text{surface sites}}$) = $3.5 \text{ Mo atoms} / 3.13 \times 10^{-19} \text{ m}^2 = 1.12 \times 10^{19} \text{ Mo atoms m}^{-2}$.

The calculation of TOF_{BET} is based on SSA of the $\text{Mo}_2\text{C}/\text{C}_{\text{support}}$ sample.^[14] First we determine the total number of surface Mo atoms ($n_{\text{Mo atom}}$) presence in the active material (e.g. Mo_2C)

$$= (1.12 \times 10^{19} \text{ Mo atoms m}^{-2}) \times m_{\text{loading}} \times (\text{wt}\%_{\text{Mo}_2\text{C}}/100) \times A_{\text{BET}} \quad [\text{Equation 1}]$$

where

- m_{loading} is the mass loading of sample on the electrode disk [$2 \times 10^{-5} \text{ g}$]

- ii. $wt\%_{\text{Mo}_2\text{C}}$ is the weight percentage of Mo_2C in $\text{Mo}_2\text{C}/\text{C}_{\text{support}}$ sample [wt%]. Please refer to Table A.3 for the value.
- iii. A_{BET} is the SSA of the sample [$\text{m}^2 \text{g}^{-1}$]. Please refer to Table A.4 for the value.

Next we determine the TOF_{BET} by assuming that all the Mo sites are involved in the HER,

$$\text{TOF}_{\text{BET}} = (j \times A_{\text{disk}} \times N_{\text{A}}) / (F \times z \times n_{\text{Mo atom}})$$

where

- i. j is the current density from Figure 5.12a [mA cm^{-2}]. Convert [mA] to [A].
- ii. A_{disk} is the geometric surface area of the electrode disk [0.07 cm^2]
- iii. N_{A} is the Avogadro's constant [6.02×10^{23} molecules of H_2 per mole of H_2]
- iv. F is the Faraday's constant [96485 C mol^{-1}]
- v. z is the number of electrons required to form 1 molecule of H_2 [2 electrons per molecule of H_2]
- vi. $n_{\text{Mo atom}}$ is the total number of surface Mo atoms in the sample derived from equation 1 [atoms of Mo]

Calculation A.4: Determination of TOF_{RF}

The calculation of TOF_{RF} is based on roughness factor (RF) of the sample.^[15]

$$\text{RF} = C_{\text{dl of electrocatalyst}} / C_{\text{dl of flat surface}} \quad [\text{Equation 2}]$$

where

- i. $C_{\text{dl of electrocatalyst}}$ is the double-layer capacitance of electrocatalyst obtained from Figure 5.13 [mF cm^{-2}]
- ii. $C_{\text{dl of flat surface}}$ is the double-layer capacitance of flat metal carbide material [0.022 mF cm^{-2}].^[16]

Then we determine the total number of effective surface Mo atoms per cm^2 geometric area ($n_{\text{effective Mo atom}}$),

$$= (n_{\text{surface sites}}) \times \text{RF} \quad [\text{Equation 3}]$$

where

- i. $n_{\text{surface sites}}$ is the number of surface Mo sites per m^2 geometric area [$1.12 \times 10^{15} \text{ Mo atoms cm}^{-2}$].^[13]
- ii. RF is the roughness factor derived from equation 2 [no unit].

To find the TOF_{RF} we use the following formula,

$$\text{TOF}_{\text{RF}} = (j \times N_A) / (F \times Z \times n_{\text{effective Mo atom}})$$

where

- i. j is the current density from Figure 5.12a [mA cm^{-2}]. Convert [mA] to [A].
- ii. N_A is the Avogadro's constant [6.02×10^{23} molecules of H_2 per mole of H_2]
- iii. F is the Faraday's constant [96485 C mol^{-1}]
- iv. z is the number of electrons required to form 1 molecule of H_2 [2 electrons per molecule of H_2]
- v. $n_{\text{effective Mo atom}}$ is the total number of surface effective Mo atoms in the sample derived from equation 3 [atoms of Mo per cm^2 geometric area]

In this work, the TOF_{RF} value is smaller than TOF_{BET} value and the former one is defined as the lower bound and the latter is defined as upper bound.

The TOF average (TOF_{ave}) is being represented as $(\text{TOF}_{\text{RF}} + \text{TOF}_{\text{BET}})/2$.

Calculation A.5: Determination of Faraday efficiency

We use the following equation to calculate the Faraday efficiency,

$$\text{Faraday efficiency} = (\text{number of mole of measured } \text{H}_2) / (\text{number of mole of theoretical } \text{H}_2) \times 100\% \quad [\text{Equation 4}]$$

First we applied a constant current of 25 mA cm^{-2} with respect to time on the working electrode and we used the Faraday's law of electrolysis to obtain the number of mole of theoretical H_2 .

$$\text{Faraday's law of electrolysis: } n_{\text{theoretical-H}_2} = (j \times A_{\text{disk}} \times t) / (F \times z) \quad [\text{Equation 5}]$$

where

- i. $n_{\text{theoretical-H}_2}$ is the number of mole of theoretical H_2 [mol]
- ii. j is the constant current density [25 mA cm^{-2}]. Convert [mA] to [A].
- iii. A_{disk} is the geometric surface area of the electrode disk [0.07 cm^2]
- iv. t is the duration of the reaction process [min]. Convert [min] to [s].

- v. F is the Faraday's constant [96485 C mol⁻¹]
- vi. z is the number of electrons required to form 1 molecule of H₂ [2 electrons per molecule of H₂]

At the same time, we collected the H₂ gas evolved from the reaction by water displacement method.^[12] Then the purity of the H₂ gas was verified using gas chromatography (GC) analysis.

The amount of H₂ gas collected [in term of volume] is then being converted to the number of mole of measured H₂ by using the ideal gas law equation.

$$\text{Ideal gas law: } n_{\text{measured-H}_2} = (P \times V) / (R \times T) \quad [\text{Equation 6}]$$

where

- i. $n_{\text{measured-H}_2}$ is the number of mole of measured H₂ [mol]
- ii. P is the atmospheric pressure [1.01325 bar]
- iii. V is the volume of H₂ gas being collected [L]
- iv. R is the universal gas constant [8.314×10^{-2} L.bar K⁻¹ mol⁻¹]
- v. T is the room temperature [298 K]

Lastly, substitute equation 5 and 6 into 4 to find the Faraday efficiency.

Appendix 3: Supplementary information for Chapter 6

Table A.5 Onset overpotentials and operating potentials at current density (j) of the electrocatalysts in this work in comparison with the reported values.

Catalyst	Onset overpotentials [V]	η (mV) at j=1, 2, 5 or 10 (mA cm ⁻²)	Reference
Commercial bulk Mo ₂ C	0.20	-240 at j=2 -310 at j=10	[6]
β -Mo ₂ C NPs	0.05-0.08	-240 at j=2	[17]
Nanoporous Mo ₂ C NWs	0.07	-200 at j=10 (1D)	[4]

Porous MoC _x nanooctahedron	0.025	-87 at j=1 -142 at j=10	[18]
MoO ₃ -MoS ₂ NWs	0.15-0.20	-240 at j=10	[19]
1T-MoS ₂ and 2H-MoS ₂ nanosheets	0.20 (1T-MoS ₂) and 0.30 (2H-MoS ₂)	-187 at j=10 (1T-MoS ₂) and -320 at j=10 (2H-MoS ₂)	[20]
MoS ₂ nanoplate	0.12	-180 at j=10	[21]
Monolayer MoS ₂ supported by NPG	0.12	-226 at j=10	[22]
NP co-doped graphene	0.29	-422 at j=10	[23]
NS co-doped graphene 500C	0.13	-276 at j=10	[24]
NS-doped Mo ₂ C nanosheets	0.046	-56 at j=1 -61 at j=2 -71 at j=5 -86 at j=10	This work

Table A.6 Summary of S dopant, N dopant, N/S dopant, C sources and Mo precursors used during hydrothermal reaction.

	S dopant	N dopant	N/S dopant	C sources	Mo precursors
Chemical name	Sodium thiosulfate	Phenylamine	Thioacetamide	Phenol	Sodium molybdate dihydrate
Chemical formula	Na ₂ S ₂ O ₃	C ₆ H ₅ NH ₂	C ₂ H ₅ NS	C ₆ H ₆ O	Na ₂ MoO ₄ ·2H ₂ O
Chemical structure

Table A.7 Element composition of the as-prepared nanosheets samples derived from CHNS elemental analyzer and ICP analysis.

Sample	Element content (mol %)			
	C	N	S	Mo
NS-doped Mo ₂ C	31.60	2.51	2.48	63.41
N-doped Mo ₂ C	31.83	5.05		63.12
S-doped Mo ₂ C	31.70		5.03	63.27
Mo ₂ C	33.76			66.24

Figure A.1 3D schematic representation of the simulated (a) unit cell and b) crystal structure of β -Mo₂C phase with an ABABAB stacking sequences consists of hexagonal structure and space group of P63/mmc with (101)-oriented in c direction.

Table A.8 HER performances of different electrocatalysts.

Catalyst	Onset potential [mV]	Tafel slope [mV dec ⁻¹]	Exchange current density [mA cm ⁻²]
Mo ₂ C	-234	75	7.9 x 10 ⁻⁴
S-doped Mo ₂ C	-144	60	3.9 x 10 ⁻³
N-doped Mo ₂ C	-186	63	1.2 x 10 ⁻³
NS-doped Mo ₂ C	-46	47	3.8 x 10 ⁻²
Pt/C	0	30	0.49

Table A.9 Summary of ΔG_{H^*} values versus the exchange current densities (i_0) of different electrocatalysts from the literature in comparison with the electrocatalysts in this work.

Electrocatalysts	ΔG_{H^*} (eV)	i_0 (A cm ⁻²)	References
Au	0.44	2.51×10^{-7}	[25]
		1.58×10^{-7}	
		3.98×10^{-6}	
Ag	0.50	1.00×10^{-5}	
		1.41×10^{-8}	
Pd	-0.15	1.00×10^{-3}	
Pt	-0.10	7.94×10^{-4}	
		2.34×10^{-3}	
		4.57×10^{-4}	
Rh	-0.11	2.51×10^{-4}	
		6.02×10^{-4}	
Ir	0.02	1.99×10^{-4}	
		3.46×10^{-4}	
Ni	-0.28	6.30×10^{-6}	
		6.16×10^{-6}	
W	-0.44	1.25×10^{-6}	
Co	-0.28	4.78×10^{-6}	
Cu	0.18	4.26×10^{-6}	
Mo	-0.38	8.51×10^{-8}	
Re	-0.33	1.34×10^{-3}	
Nb	-0.57	1.58×10^{-7}	
MoS ₂	0.08	7.94×10^{-6}	[26]
Mo ₂ C@NC	0.008	9.77×10^{-5}	[12]
com-Mo ₂ C	-0.837	1.20×10^{-6}	
Mo ₂ C@NPC/NPRGO	-0.22	1.09×10^{-3}	[27]
Zn-doped Co ₃ O ₄	-0.32	1.51×10^{-4}	[28]
MWCMNs (WO ₂ – C)	-0.22	6.45×10^{-4}	[29]
WO _{2.9}	0.01	4.07×10^{-4}	[30]
W ₂ C	-0.27	1.90×10^{-4}	This work
Fe-doped W ₂ C	-0.16	2.23×10^{-4}	
Co-doped W ₂ C	-0.05	4.07×10^{-4}	
Ni-doped W ₂ C	-0.04	7.94×10^{-4}	

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Conference presentation

[1] Hydrophilic Nitrogen and Sulfur Co-doped Molybdenum Carbide Nanosheets for Electrochemical Hydrogen Evolution.

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