Nanostructured transition metal oxide (TMO) for electrochemical devices

Khoo, Eugene

2011

Khoo, E. (2011). Nanostructured transition metal oxide (TMO) for electrochemical devices.
Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/50523>

<https://doi.org/10.32657/10356/50523>

NANYANG TECHNOLOGICAL UNIVERSITY

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

NANOSTRUCTURED TRANSITION METAL OXIDE (TMO) FOR ELECTROCHEMICAL DEVICES

by

Khoo Eugene

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

Supervisors: Assoc. Prof. Lee Pooi See and Prof. Ma Jan

School of Materials Science and Engineering

2011

Abstract

This thesis focuses on the reaction mechanism and kinetic study of electrochemical reactions in transition metal oxide, which include electrical double layer (EDL), surface charge transfer reaction and diffusion controlled redox reaction. Modifications on the oxide have been designed to study the effect on the reactions and hence the electrochemical performances. These modifications include the variation in oxide morphology and dimension, conductive metal doping and altering of oxide lattice structure. The key parameters governing the electrochemical reactions in transition metal oxides are the oxide-electrolyte interface, electronic conductivity, ion diffusion distance, ion diffusion pathway and ion intercalation site. With detailed studies in the optical and electrochemical performances of the modified oxide, the effects of altering these parameters were evaluated. The increase in oxide-electrolyte interfacial area was achieved through controlling the oxide morphology and dimension. This has promoted the surface dependent reaction (including EDL and surface charge transfer reaction). As a result, higher electrochemical activity can be achieved and hence higher capacitance and rate capability. On the other hand, the electronic conductivity was shown to be improved through doping conductive metal into the oxide lattice. The enhancement in the electronic conductivity improves charge transfer rate in the oxide, resulting in better rate capability and capacitance. Ion diffusion strongly affects the diffusion controlled redox reaction in oxide lattice. The ion diffusion distance and diffusion pathway are the two basic factors of ion diffusion in oxide lattice. In this thesis, the shortening of diffusion distance has been achieved by reducing the oxide dimension while different types of diffusion pathways with shortened diffusion distances were generated through the altering of oxide lattice structure. The last

parameter is the ion intercalation sites, which were tailored through controlling the oxide lattice structure. By having large amount of easy accessible intercalation sites, the chemisorptions of cation at oxide-electrolyte interface and the ion intercalation in oxide lattice were greatly promoted. This increases the total amount of redox reaction in the oxide. In parallel to the mechanism studies, these modified oxides were employed as the electrodes of electrochromic (EC) device and supercapacitor to examine their EC properties and the charge storage performances.

Acknowledgement

First and foremost, I would like to express my sincere appreciation to my supervisors, Associate Professor Lee Pooi See and Professor Ma Jan for their support in my Ph. D program. I am very fortunate and honoured to have such understanding and supportive supervisors. It has been a very valuable learning experience to work under their supervision. I have benefited tremendously from their knowledge as a scientist, advisor, and also as a person. It has indeed been an absolute privilege and honor to have worked and studied under their guidance.

I also would like to specially thank Professor Bruce Dunn, Professor Katherina Al-Shamery, Dr. John Wang, Dr. Yan Jian, Dr. Wang JinMin, Afriyanti Sumboja, Wang Xu, Maraike Ahlf, Jorg Stover and other group members for their professional knowledge and always being helpful throughout the Ph. D program.

Last but not least, I would like to thank my dear family and friends, for their support and encouragement throughout my studies. Without them being so supportive, understanding, and caring, I would not have had such enjoyable studies.

Table of content

Content	Page
Abstract	i
Acknowledgement	iii
Table of Content	iv
List of Figures	vi
List of Tables	xi
Publication list	xii
Chapter 1 Introduction	
1.1 Background	1
1.2 Research objectives and scope	3
1.3 Organization of the thesis	4
Chapter 2 Literature Reviews	
2.1 Electrochemical reactions in transition metal oxides	6
2.2 Electrochemical devices: Electrochromic (EC) device and supercapacitor	17
2.3 Summary	31
Chapter 3 Methodology	
3.1 Synthesis of mesoporous WO ₃ film	35
3.2 Synthesis of un-doped V ₂ O ₅ nanobelts	36
3.3 Synthesis of Ag doped V ₂ O ₅ nanobelts	37
3.4 Synthesis of Na doped V ₂ O ₅ nanobelts	37
3.5 Structural characterization	38
3.6 Electrochemical studies	39
3.7 Optical studies	40
Chapter 4 Morphology effects on electrochemical reactions and electrochromic (EC) performances in transition metal oxide	
4.1 Introduction	42
4.2 Structural characterization of non-porous and macroporous oxide film	47
4.3 Studies of redox reaction and charge intercalation in mesoporous and non-porous oxide film	49
4.4 Studies of optical modulation and colour switching in mesoporous and non-porous oxide film	51

4.5 Effects of oxide morphology and dimension on optical and electrical responses	56
4.6 Effects of oxide morphology and dimension on solid state ion diffusion in oxide lattice	60
4.7 Effects of oxide morphology and dimension on ion intercalation	64
4.8 Summary	67
Chapter 5 Effects of metal doping on electrochemical reactions and charge storage in transition metal oxide	
5.1 Introduction	68
5.2 Structural characterization of V ₂ O ₅ based nanobelts	71
5.3 Electrochemical redox reactions and charge storage in metal doped V ₂ O ₅ nanobelts	75
5.4 Electrochemical redox reaction in metal doped V ₂ O ₅ nanobelts	80
5.5 Surface dependent and diffusion controlled redox reaction in metal doped V ₂ O ₅ nanobelts	86
5.6 Electron and ion transportation in the un-doped and metal doped V ₂ O ₅ nanobelts	92
5.7 Coupling the effects from oxide dimension and metal doping	97
5.8 Summary	104
Chapter 6 Effects of oxide lattice structure on electrochemical reactions and charge storage in transition metal oxide.	
6.1 Structural Characterization of the Na doped V ₂ O ₅ nanobelts	107
6.2 Structural characterization on Na doped V ₂ O ₅ nanobelts	111
6.3 Formation of β -Na _{0.33} V ₂ O ₅ nanobelts	113
6.4 Layered structure and framework structure of Na doped V ₂ O ₅ nanobelts	117
6.5 Electrochemical reaction and charge storage in layered and framework structure	122
6.6 Surface dependent reaction and diffusion controlled reaction in layered and framework structure Na doped V ₂ O ₅ nanobelts	126
6.7 Summary	129
Chapter 7 Conclusion and future works	
7.1 Summary	130
7.2 Recommendations for future work	134
References	136

List of Figures

Figure	Caption	Page
2.1	Schematic view of a three-electrode electrochemical cell.	6
2.2	Schematic view of the (a) electrical double layer (EDL) at oxide-electrolyte interface ³ and (b) the proposed model of the EDL where the anions are specifically absorbed. ⁴	8
2.3	Redox reactions at the (a) oxide-electrolyte interface and (b) bulk oxide.	11
2.4	Schematic views of ion intercalation in transition metal oxide working electrode.	13
2.5	Schematic views of of charge carriers (electrons and ions) population in the transition metal oxide during ion de-intercalation.	14
2.6	Schematic view of EC device ¹³	18
2.7	The principle of electrochromic devices. Arrows indicate the incoming and outgoing light wave (thickness of arrow - the light intensity, blue-colored, white-bleached).	19
2.8	Ragone Plot for energy density and power density of energy storage devices.	25
2.9	Schematic view of (a) electrical double layer capacitor (EDLC) and (b) the charge separation in EDLC. ^{3,5}	26
2.10	Specific capacitances (SC) of potential transition metal oxide candidates for supercapacitor electrode material: RuO ₂ ^{50, 66-69} , V ₂ O ₅ ^{19, 35, 52-54} , MnO ₂ ^{56, 57, 62, 70, 71} , Mn ₃ O ₄ ^{60, 72} , Co ₃ O ₄ ⁷³⁻⁷⁵ , SnO ₂ ^{76, 77} .	28
3.1	Correlation between the oxide modification, demonstrated application and target key parameters of electrochemical reactions in transition metal oxide.	35
4.1	(a) Cation intercalation at coloration state, (b) cation de-intercalation at bleaching state, (c) octahedral intercalation site in WO ₃ .	45
4.2	(a) Schematic view of WO ₃ electrodeposition with and without polystyrene (PS) template, (b) FESEM image of the PS template on the ITO substrate [Inset: the diameter distribution of PS spheres], (c) macroporous WO ₃ film after PS removal in toluene, (d) non- porous WO ₃ film.	47
4.3	Cyclic voltammograms of the macroporous and non-porous WO ₃ film at 100 mV s ⁻¹ scan rate. (Electrolyte: 1 M LiClO ₄ /PC).	49
4.4	UV-Vis transmittance spectra of the (a) non-porous and (b) macroporous WO ₃ film at coloration and bleaching state.	51
4.5	(a) Step voltage of ± 2.5 V applied on WO ₃ films, transmittance spectra of the (b) non-porous and (c) macroporous WO ₃ film at coloration and bleaching state (at 633 nm).	55
4.6	The plot of normalized transmittance vs. current for (a) non-porous and (b) macroporous WO ₃ film during coloration.	56

4.7	Charge density dependence of optical density (OD) of (a) non-porous and (b) macroporous WO ₃ film. The coloration efficiency (CE) is evaluated from the linear region of the curve.	58
4.8	(a) The time dependence of $Q(t)t^{-1/2}$ for the four voltage steps ranging from -0.15 V to -0.35 V (vs. Ag/AgCl), (b) the diffusion coefficient in macroporous and non-porous WO ₃ film.	63
4.9	Schematic views of the (a) non-porous and (b) macroporous WO ₃ during the Li ⁺ intercalation.	65
5.1	FESEM and TEM (insets) images of (a) un-doped and (b) Ag doped V ₂ O ₅ nanobelts, (c) EDX spectrum of un-doped V ₂ O ₅ and Ag doped V ₂ O ₅ nanobelts.	71
5.2	Schematic view of ion diffusion distance in nanobelts structure with (a) thickness and (b) width perpendicular to the electric field.	72
5.3	X-ray diffraction (XRD) patterns of un-doped and Ag doped V ₂ O ₅ nanobelts.	73
5.4	Thermal-gravimetric analyses (TGA) of un-doped and Ag doped V ₂ O ₅ nanobelts in N ₂ ambient. The heating rate is 10 °C min ⁻¹ .	74
5.5	Cyclic voltammograms of un-doped and Ag doped V ₂ O ₅ nanobelts at 5 mV s ⁻¹ scan rate. Electrolyte: 1.0 M LiClO ₄ /PC.	76
5.6	Scan rate dependence specific capacitance of un-doped and Ag doped V ₂ O ₅ nanobelts for scan rate ranging from 5 mV s ⁻¹ to 100 mV s ⁻¹ . Electrolyte: 1.0 M LiClO ₄ /PC.	77
5.7	CV curve of Ag doped V ₂ O ₅ nanobelts at 5 mV s ⁻¹ scan rate. The samples are charged or discharged to different oxidation and reduction voltages as shown in the figure before subjected to XPS analysis. Electrolyte: 1M LiClO ₄ /PC.	80
5.8	High resolution XPS spectra for (a) O 1s and V 2p and (b) Ag 3d region of samples at (Red -0.1 V) and (Red -0.4 V).	82
5.9	High resolution XPS spectrum for (a) O 1s and V 2p and (b) Ag 3d region of sample (Ox -0.1 V) and (Ox +0.2 V).	84
5.10	Voltammetric responses of the (a) un-doped and (b) Ag doped V ₂ O ₅ nanobelts at 5 mV s ⁻¹ . The shaded region is contributed by the surface dependent reaction while the white region under the CV curve corresponds to the diffusion controlled reaction.	88
5.11	Specific capacitance (SC) contribution from surface dependent reaction and diffusion controlled reaction at 5 mV s ⁻¹ .	89
5.12	I-V testing of single nanobelt (deposited across Au electrodes): a) Un-doped nanobelt and b) Ag doped nanobelt. [Insets: the FESEM images of the single nanobelt on Au electrode.]	93
5.13	I-V plot of single nanobelt: a) Un-doped nanobelt and b) Ag doped nanobelt at forward bias.	94
5.14	The diffusion coefficients in un-doped and Ag doped V ₂ O ₅ nanobelts for five voltage steps.	95
5.15	FESEM and TEM (insets) images of (a) 150 °C and (b) 120 °C synthesized Ag doped V ₂ O ₅ nanobelts, (c) EDX spectrum of 150 °C and 120 °C synthesized Ag doped V ₂ O ₅ nanobelts.	98
5.16	a) X-ray diffraction (XRD) patterns and (b) thermal-	99

	gravitational analysis (TGA) of 150 °C and 120 °C synthesized Ag doped V ₂ O ₅ nanobelts.	
5.17	a) Cyclic voltammograms and (b) scan rate dependence specific capacitance (SC) of 150 °C and 120 °C synthesized Ag doped V ₂ O ₅ nanobelts.	101
5.18	Voltammetric responses of (a) 150 °C and (b) 120 °C synthesized Ag doped V ₂ O ₅ nanobelts at 5 mV s ⁻¹ , (c) relative ratio between surface dependent capacitance and intercalation capacitance.	103
6.1	Oxide lattice structure of layered V ₂ O ₅ based material (a) along y axis and (b) with intercalated substance (hollow circles) between VO ₅ layers. ¹¹⁴	109
6.2	Oxide lattice structure of framework V ₂ O ₅ based material (along direction [010]). ¹⁵⁰	110
6.3	X-ray diffraction patterns of as-synthesized and annealed Na doped V ₂ O ₅ .	111
6.4	FESEM images of the Na doped V ₂ O ₅ nanobelts (a) before and (b) after annealing.	112
6.5	Thermal-gravimetric analysis (TGA) of the Na doped V ₂ O ₅ nanobelts from room temperature to 500 °C in N ₂ ambient at heating rate of 10 °C per minute.	113
6.6	X-ray photoelectron spectroscopy (XPS) spectra of as-synthesized and annealed Na doped V ₂ O ₅ nanobelts: (a) wide range scanning and (b) high resolution spectra at V 2p and O 1s region.	115
6.7	Phase diagram of M _x V ₂ O ₅ bronze (In this phase diagram, the doping ion is Li). ^{114, 151}	117
6.8	Transformation process from layered structure to framework structure in V ₂ O ₅ based system (a) slicing the VO ₅ layers into slabs 1 and 2 by crystallographic shear and (b) re-arrangement of the slabs and forming framework structure. ¹⁵¹	119
6.9	The intercalation sites within the tunnel of the β-phase framework structure (a) intercalation site at the middle of the tunnel (M ₁ site), (b) eight coordinated site (M ₂ site) and (c) tetrahedral site (M ₃ site). The solid circle represents the intercalated cation while the hollow circle represents the oxygen atoms. ¹⁵⁰	120
6.10	Cyclic voltammograms of layered and framework structure Na doped V ₂ O ₅ nanobelts. Electrolyte: 1 M LiClO ₄ /PC.	122
6.11	Scan rate dependence specific capacitances (SC) of layered and framework structure Na doped V ₂ O ₅ nanobelts.	124
6.12	Voltammetric responses of (a) layered and (b) framework structure Na doped V ₂ O ₅ nanobelts at 5 mV s ⁻¹ scan rate. The solid line represents the total current. The shaded region is contributed by the surface dependent reaction while the white region is contributed by the diffusion controlled reaction. (c) Relative SC contribution from surface dependent reaction and diffusion controlled reaction.	126

List of Tables

Table	Caption	Page
2.1	The key parameters of the oxide and the corresponding electrochemical reaction.	34
4.1	Destructive and constructive interference for wavelength between 350 nm to 500 nm and the corresponding travel distance in the pore.	53
4.2	Li^+ diffusion coefficient in WO_3 .	64
5.1	Various dopants in V_2O_5 and the dopant's electronic conductivity and ionic radius. The values in bold are the three highest ionic radius and electronic conductivity.	70
5.2	Electronic conductivities and diffusion coefficients of Li^+ of 150 °C and 120 °C synthesized Ag doped V_2O_5 nanobelts.	100

Publication List

1. Electrochemical Energy Storage in a beta- $\text{Na}_{0.33}\text{V}_2\text{O}_5$ Nanobelt Network and its Application for Supercapacitors
E. Khoo, J. M. Wang, J. Ma and P. S. Lee
Journal of Materials Chemistry **20**, 8368 (2010)
2. Charge Storage Mechanisms in Silver doped Vanadium Oxide Nanobelts for Supercapacitor Application
E. Khoo, A. Sumboja, J. Stöver, K. Al-Shamery, J. Ma and P. S. Lee
Submitted (2011)
3. Electrophoretic Deposition (EPD) of WO_3 Nanorods for Electrochromic Application
E. Khoo, P. S. Lee and J. Ma
Journal of the European Ceramic Society **30**, 1139 (2010)
4. Coating of Manganese Oxide on Tin Oxide Nanowires with High-performance Capacitive Behaviour.
J. Yan, **E. Khoo**, A. Sumboja and P. S. Lee
ACS Nano **4**, 4247 (2010)
5. Controlled Synthesis of WO_3 Nanorods and Their Electrochromic Properties in H_2SO_4 Electrolyte.
J. M. Wang, **E. Khoo**, P. S. Lee and J. Ma
Journal of Physical Chemistry C **113**, 9655 (2009)
6. Synthesis, Assembly, and Electrochromic Properties of Uniform Crystalline WO_3 Nanorods
J. M. Wang, **E. Khoo**, P. S. Lee and J. Ma
Journal of Physical Chemistry C **112**, 14306 (2008).

Conference presentation

1. Annealing Effect on Hydrothermal Synthesized Vanadium Oxide (V_2O_5) Nanobelts and its Electrochemical Capacitance (*Oral Presentation*)
E. Khoo, J. M. Wang, P. S. Lee and J. Ma
MRS Fall, Symposium S: Solid-State Ionics [Boston (USA), 1-5 Dec 2008]
2. Vanadium Oxide (V_2O_5) Nanobelts for Supercapacitor Applications (*Oral Presentation*)
E. Khoo, J. Ma and P. S. Lee
ICMAT 2009, Symposium F - Nanostructured Materials for Electrochemical Energy Systems: Lithium Batteries, Supercapacitors and Fuel Cells [Singapore, 28 Jun – 3 Jul 2009]

Chapter 1 Introduction

1.1 Background

Electrochemical reactions in transition metal oxide (TMO) have created interesting optical and electrochemical properties which can be utilized as the working electrode in electrochemical devices such as energy storage device (battery and supercapacitor) and electrochromic (EC) device (smart window and anti-glare rare view mirror). Increasing stringent requirements in device performance have arisen with the advancement in technology. The working electrode has to be improved for better rate capability and larger capacitance. Modifying the oxide to promote the electrochemical reaction is reckoned to be one of the major directions to address the challenges. The modifications need to be designed based on the electrochemical reaction mechanism in transition metal oxide with the objective of solving the rate limiting issues in the oxide.

Upon voltage biasing, the redox reaction can be reversible or quasi-reversible. The redox reaction in transition metal oxide (MeO_n) can be expressed as:

Upon the electron injection (left hand side), cation M^+ in the electrolyte will be attracted into the oxide to maintain charge neutrality. This process is referred as “electron-ion double injection”. Simultaneously, the transition metal ion (Me) is partially reduced (The reduced transition metal ion corresponds to the electron insertion level x) and the final product is the formation of bronze (M_xMeO_n). Oxidation takes place upon the extraction of electrons. The oxidation state of

transition metal ion is increased with an electric field being built up across the oxide and expels the previously intercalated cations.

In transition metal oxide, the redox reaction in the surface and bulk of the oxide exhibit different reaction mechanism. At the oxide surface, or more precisely: the oxide-electrolyte interface, the solvated cations in the electrolyte attach onto the interface during the electron injection and charge transfer process takes place as Equation 1.1. This reaction is surface dependent and exhibits capacitive response. On the other hand, the redox reaction in the bulk oxide involves the ion intercalation and de-intercalation process. During the electron injection, the cations in the electrolyte are also injected across the oxide-electrolyte interface and intercalated adjacent to the reduced transition metal ion (in the interior part of the oxide). This redox reaction is a diffusion controlled reaction and exhibits slower kinetic as compared to the charge transfer process at the oxide-electrolyte interface. Hence, although the redox reaction in transition metal oxide can provide interesting and promising optical and electrochemical performances, the slow reaction rate in bulk oxide electrode can pose as a limitation to its performance.

Research efforts have been carried out in transition metal oxides to improve the rate capability while preserving the unique optical and electrochemical properties associated with the redox reaction. The most direct method is the modifying of the oxide to facilitate and promote the redox reaction. It is noted that the reaction mechanism and kinetic of the modified oxides can be altered via several key parameters. However, inappropriate variations could, on the other hand, deteriorate the performance if the modification is not optimized. Hence, systematic studies on the reaction mechanism, kinetics and the resultant effects are required. Promising oxide

electrode for electrochemical devices can then be designed with the in-depth understandings on the reaction mechanism and the reaction key parameters.

1.2 Research objectives and scope

The main objective of this research is to explore strategies to enhance the rate capability and the amount of electrochemical reaction per unit mass of transition metal oxides, which are the two fundamental properties that govern the optical and electrochemical performances. In order to achieve these goals, it is essential to understand in the electrochemical reaction mechanism and kinetics in the oxides. Through the altering of the key parameters of the electrochemical reaction, in-depth understandings can be achieved. The resultant strategies can also be employed in the next generation of TMO electrode in electrochemical devices for faster reaction rate and better performance.

In this thesis, three modifications on the transition metal oxide electrode have been demonstrated with consideration on their effects to five key parameters of electrochemical reactions. The parameters include the oxide-electrolyte interface, ion diffusion distance, electronic conductivity, ion diffusion pathway and ion intercalation sites. Through modification of the oxide structures, these parameters can be altered to achieve faster reaction rate or increase in redox reaction. The first approach is the altering of the oxide morphology and dimension through the controlling of synthesis conditions. This approach aims to increase the reaction sites for surface dependent electrochemical reactions and create short ion diffusion distances to facilitate the diffusion controlled reactions. The second structural modification is the doping of conductive metal ion into the oxide lattice. The goal is to enhance the electronic

conductivity of the transition metal oxide and hence the reaction rate of the electrochemical reactions. The final strategy is the tailoring of the oxide lattice structure. This is to allow easy accessible diffusion pathways and ion intercalation sites to facilitate the ion diffusion and intercalation processes. Structural characterizations were then carried out and correlated to the optical and electrochemical performances. The results of these studies serve as the foundation for synthesizing transition metal oxide with promising rate capability and capacitance.

The tailored oxides have been evaluated as the electrodes for electrochemical devices such as electrochromic (EC) device and supercapacitor. The corresponding optical and electrochemical performances of the oxide electrodes were benchmarked to the state of art electrochemical devices as a verification that the approaches are practical and suitable to be employed in the electrochemical devices.

1.3 Organization of the thesis

Chapter 1 provides an overview on the electrochemical reaction in transition metal oxide and the basic operating mechanism of the oxide as working electrode of electrochemical devices. The objectives and scope of this thesis are also defined with the goal of providing strategies to circumvent the limitation in transition metal oxides for improved optical and electrochemical performances. In Chapter 2, detail discussions in the reaction mechanism of three main types of electrochemical reactions in TMO are presented. The state of art of electrochemical devices, namely, the electrochromic (EC) device and supercapacitor are also reviewed. Five key parameters which govern the oxide rate capability and charges are proposed based on the reviews. Chapter 3 presents the methodology and experimental procedures of

synthesizing the modified oxide electrode, structural characterization, optical and electrochemical testing. The result and discussion, the correlation between the reaction's key parameters and enhanced performances are presented in Chapter 4, 5 and 6. In Chapter 4, comparison between non-porous and macroporous WO_3 film is carried out to show the amount of redox reaction and rate capability can be significantly improved by creating more reaction site and shortening the ion diffusion distance. Chapter 5 demonstrates the doping in V_2O_5 nanobelts, which has improved the electronic conductivity and charge transfer rate in the oxide. The Ag doped nanobelts are employed as the working electrode of supercapacitor and the reaction mechanism is studied based on the different time dependence of the three electrochemical reactions. An example of coupling the modification reported in Chapter 4 and 5 is also discussed in the last section of Chapter 5 to demonstrate the potential synergistic effects. In chapter 6, detail studies are carried out to investigate the effects of oxide lattice structure on the electrochemical reactions. The studies mainly focused on the ion diffusion pathway and ion intercalation site in the oxide lattice, which expect to have significant effect on the cation chemisorption (at the oxide-electrolyte interface), ion diffusion and ion intercalation process. Lastly, Chapter 7 summarizes the findings in previous chapters and proposes recommendations for future work.

Chapter 2 Literatures reviews

2.1 Electrochemical reactions in transition metal oxides (TMO)

2.1.1 Electrochemical cell

Figure 2.1 *Schematic view of a three-electrode electrochemical cell*

Electrochemical cell is composed of three main components: conductive substrate, active material and electrolyte. The conductive substrate acts as the injection and extraction pathway of electrons while the electrolyte contains ions (cation or anion) for electrochemical reaction. The active material determines the type of electrochemical reaction and hence the functions of the electrochemical cell. In this thesis, three-electrode cell setup is employed for electrochemical studies. Figure 2.1 shows the schematic view of the three-electrode electrochemical cell, which composed of working electrode (WE), reference electrode (REF) and counter electrode (CE). The working electrode contains the active material and its electrical signal (upon voltage biasing) is monitored to study the electrochemical reaction. In this thesis, the working electrode is a ITO glass coated with a layer of specially

modified transition metal oxide. The reference electrode is a standardize electrode which serves as the reference for the applied voltage. The reference electrode provides accurate voltage reading during the electrochemical study, which is important for applying voltage and voltage reading during the electrochemical studies and actual application. The counter electrode is basically a current collector and has to be stable in the electrolyte during the electrochemical reaction. The three electrodes are immersed in an ionic conductive electrolyte, which is usually in liquid form. During the electrochemical reaction, the electrolyte is assumed to be only ionic conductive and no electron can flow through the electrolyte. The three electrodes are externally connected to a potentiostat / galvanostat. The voltage or current are applied from the potentiostat / galvanostat to the working electrode and the corresponding current or voltage feedback signal are collected. In transition metal oxide, there are mainly three types of electrochemical reactions that take place at the surface or interior of the active materials upon voltage biasing, which will be discussed in detail in the next section.

2.1.2 Electrochemical reactions

When the transition metal oxide is subjected to voltage biasing, three types of electrochemical reactions occur at the oxide-electrolyte interface or the bulk of the oxide. Charges (q) are involved in these electrochemical reactions across the applied voltage (V) and contribute capacitance (C). Since the current and charges vary with the voltage during the electrochemical reaction, the induced capacitance should be expressed as a differential capacitance:

$$C = dq/dV \tag{2.1}$$

The capacitance is an important criterion because it reflects the charge storage capability of the TMO and is the basis of several electrochemical properties, such as specific capacitance (SC) and energy density ($E=1/2CV^2$). Rate capability and reaction kinetic can also be evaluated through the capacitance as the capacitance at a specific charge-discharge rate is affected by these two properties.

The capacitance in TMO is contributed by three electrochemical reactions, namely electrical double layer (EDL), redox reaction at the oxide-electrolyte interface and diffusion controlled redox reaction in the bulk oxide.^{1, 2}

Figure 2.2 Schematic view of the (a) electrical double layer (EDL) at oxide-electrolyte interface³ and (b) the proposed model of the EDL where the anions are specifically absorbed.⁴

Figure 2.2 illustrates the schematic view of the electrical double layer (EDL) at the oxide-electrolyte interface, which is electrostatic in nature. When a voltage bias is applied to the oxide, charges accumulate at the oxide surface and the oppositely charged species in the electrolyte are specifically absorbed onto the oxide-electrolyte

interface and form an “inner” layer. This layer is called the Helmholtz or Stern layer. The locus of the electrical centres of these specifically absorbed ions is called the inner Helmholtz plane (IHP), which is at a distance x_1 from the interface. After the formation of inner layer, solvated ions in electrolyte can approach the oxide to a distance x_2 and form a second layer. The locus of these solvated ions is called the outer Helmholtz plane (OHP). This layer holds the maximal charge density and is the centre of the solvated ions.^{3, 4} These two layers are referred as the electrical double layer (EDL) and a double layer capacitance exists because charges can be stored in the EDL. The EDL is a surface dependent reaction with capacitive response, which is beneficial for an electrochemical device. Since the reaction only involves simple charge separation at the interface, the EDL exhibits fast reaction rate as the conventional electrostatic capacitor.⁵ Moreover, the reaction only occurs at the interface, the electrode material will not suffer stress induced by the ion intercalation and de-intercalation. This helps to achieve a longer lifespan for the electrode material. However, the double layer capacitance is typically in the range of 15 to 50 $\mu\text{F cm}^{-2}$ in aqueous electrolyte and even smaller in the non-aqueous electrolyte^{3, 4, 6}, which can only contribute insignificant capacitance for bulk electrode as the electrode-electrolyte interfacial area is small. In order to increase the total charge (i.e. capacitance), porous materials with high surface to volume ratio have been employed as the electrode. For example of utilizing an 50 $\mu\text{F cm}^{-2}$ electrode material with surface area of 1000 $\text{m}^2 \text{g}^{-1}$, a high capacitance of 500 F g^{-1} can be achieved. This concept has been utilized in the electrical double layer capacitor (EDLC), which is already a commercially available energy storage device. Carbons based materials with large surface area above 500 $\text{m}^2 \text{g}^{-1}$ have been employed in EDLC.^{3, 5, 7} The large surface area helps to achieve a promising amount of charge and capacitance, while

maintaining a promising rate capability and good cycling stability. However, the actual capacitance in EDLC is usually smaller than the theoretical calculated capacitance as the ion accessibility in carbon material is affected by the pore size and pore structure. Hence, the actual electrochemical active surface area is normally smaller than the surface area estimated through Brunauer-Emmett-Teller (BET) method.

Besides EDL, redox reaction also occurs in transition metal oxide upon the voltage biasing. The redox reaction takes place at transition metal ion and is stimulated by the injection or extraction of electron, it is the main electrochemical reaction in transition metal oxide. The reaction in transition metal oxide (MeO_n) can be expressed as:

where M is the mono-valence cation intercalated or absorbed in the oxide and x stands for the electron insertion level and cation intercalation level. The altering in transition metal ion during the redox reaction has induced unique optical and electrochemical properties which can be applied in electrochemical devices. In this thesis, electrochromic (EC) device operates based on the different colour at respective oxidation state of transition metal ion while the supercapacitor utilizes the electrochemical energy stored during the charge carriers' movement.

Figure 2.3 Redox reactions at the (a) oxide-electrolyte interface and (b) bulk oxide.

There are two kinds of redox reaction in transition metal oxide (Figure 2.3). The first redox reaction is the charge transfer process at the oxide-electrolyte interface, which is a surface dependent redox reaction.^{1, 6} Charge transfer takes place between surface transition metal ions and the solvated ions in the electrolyte. Solvated ions are attracted towards or being expelled from the oxide-electrolyte interface depending on the applied voltage and the resultant electrode polarity. This surface redox reaction at the oxides (MeO_n) can be expressed as:

The free surface sites of oxide (MeO_n) absorb the cation M^+ and form the bronze ($M \cdot MeO_n$). If the occupied surface site (i.e. $M \cdot MeO_n$) has fractional surface coverage of θ , the free surface site is then $(1 - \theta)$ and the equilibrium situation at potential V can be expressed as:⁶

$$\frac{\theta}{1-\theta} = \frac{k_1 C_{M^+}}{k_{-1}} \exp(-VF/RT) \quad (2.4)$$

where k_1 and k_{-1} are the rate constant for forward and backward reaction, respectively. C_{M^+} is the concentration of M^+ ion. F , R and T stand for the Faraday constant, gas constant and the temperature. Rearrange the formula for θ :

$$\theta = \frac{KC_{M^+} \exp(-VF/RT)}{1 + KC_{M^+} \exp(-VF/RT)} \quad (2.5)$$

where $K (=k_1/k_{-1})$ is equilibrium constant for the absorption of M^+ with charge transfer. Equation 2.5 shows that this surface redox reaction is strongly affected by the applied voltage V . The reaction is a continuous function of the applied voltage V for $\theta = 0$ to $\theta \rightarrow 1$ with peak value of θ occurs at a specific voltage.⁶ Since the reaction takes place at the interface, this reaction is a surface dependent reaction and exhibit fast reaction kinetic and capacitive response as EDL. Hence, electrode with large oxide-electrolyte interfacial area is beneficial for the surface dependent redox reaction as the more reaction sites will be created and the reaction will be promoted.

The second redox reaction is diffusion controlled redox reaction which takes place within the oxide lattice and involving the solid state ion diffusion. The ion movement at reduced and oxidized state of the transition metal ions are described and ion “intercalation” and ‘de-intercalation’, respectively.

Figure 2.4 Schematic views of ion intercalation in transition metal oxide working electrode.

Figure 2.4 illustrates the ion intercalation process in transition metal oxide during the diffusion controlled redox reaction, where the electron-ion double injection occurs upon voltage biasing. When electrons are injected into the transition metal oxide through the conductive substrate and partially reduce the transition metal ion, the oxide layer is negatively charged by these injected electrons and an electric field is built up between counter electrode and transition metal oxide. Cations in the electrolyte will be attracted by the negatively charged electrode and diffuse along the electric field towards the oxide-electrolyte interface. In order to maintain the charge neutrality, the cations will be injected across the oxide-electrolyte interface, diffuse in the oxide lattice and then intercalated adjacent to the reduced transition metal ions (Figure 2.4). It should be noted that the working electrode structure has implied boundary conditions for the electrons and ions during the intercalation process. Consider an oxide layer of thickness d , ions can only diffuse in the electrolyte and being injected into the oxide and stop at the oxide-substrate interface ($x=d$) while

electrons can only be injected from the conductor and stop at the oxide-electrolyte interface ($x=0$) due to the low electronic conductivity of the electrolyte (Figure 2.4).

Figure 2.5 Schematic views of of charge carriers (electrons and ions) population in the transition metal oxide during ion de-intercalation.

Figure 2.5 illustrates the ion de-intercalation process and charge carriers population in the transition metal oxide after the electron-ion double injection. Ion de-intercalation occurs when the electrons are extracted from transition metal oxide. The transition metal ions will be oxidized and the cations are simultaneously expelled back to electrolyte. Similar to the intercalation process, the ions have to diffuse across the oxide layer and pass through the oxide-electrolyte interface. After the ion intercalation, the oxide is assumed to be full with uniformly distributed neutral electron-ion plasma. Similar to the ion intercalation process, there is also some boundary conditions for the electrons and ions during the ion de-intercalation: the electrons only leave the oxide layer through the conductor while ions can only be expelled back to the ionic electrolyte. After the de-intercalation process is initiated, the oxide layer can be further divided into regions I, II and III (as shown in Figure 2.5) according to the

electron-ion population. Upon voltage bias, the ions in region III ($x_2 < x < d$) will be expelled toward the electrolyte and leave behind the electrons. Similarly, electrons in region I ($0 < x < x_1$) will be attracted towards the conductor and leave behind the cations. Region II contains the neutral electron-ion plasma, this region will diminish and region I and II will grow until all electrons and ions are extracted from the oxide layer.

In summary, the second redox reaction is a diffusion controlled reaction. The main concern of this reaction is the diffusion time as it governs the reaction kinetic and rate capability of the transition metal oxide. As shown in Figure 2.4 and 2.5, the maximum ion diffusion distance is the thickness of the oxide layer. Long diffusion time would be required for thick oxide layer (i.e. bulk oxide) and the whole redox reaction will become sluggish. Fortunately, the diffusion distance can be significantly reduced in mesoporous oxide or oxide nanostructures. These specifically modified oxides are surrounded by the ionic electrolyte and the ion can be injected into the oxide through all the oxide-electrolyte interfaces. The ion diffusion distance, instead of the whole oxide layer thickness, is now only the wall thickness of mesoporous oxide ⁸ or the nanoscale dimension in nanostructures. ^{9, 10}

In summary, three electrochemical reactions take place in transition metal oxide upon voltage biasing, namely EDL, surface charge transfer process and diffusion controlled redox reaction. The redox reaction (including surface charge transfer reaction and diffusion controlled reaction) is the main reaction in transition metal oxide and has generated attractive optical and electrochemical properties for actual application. Due to the different reaction mechanism, the EDL, surface redox reaction (surface charge transfer reaction) and diffusion controlled redox reaction exhibit different rate dependence: the surface charge transfer reaction is inversely proportional to time while the diffusion controlled reaction is inversely proportional to the square root of

time.¹¹ Generally, the diffusion controlled redox reaction is slower than the surface dependent redox reaction and EDL as the slow ion diffusion has limited the reaction kinetic. These characteristic are very useful for designing the device working electrode and experiments can be designed based on these characteristic to study the ion diffusion process and redox reaction.^{1, 12}

2.2 Electrochemical devices: Electrochromic (EC) device and supercapacitor

Transition metal oxides have been employed as the active material in the working electrode for electrochemical devices due to its unique characteristics, namely: 1) multi-valence transition metal ion for redox reaction, 2) reversible redox reaction where the transition metal ion can be reversibly reduced and oxidized upon voltage biasing, 3) different colours which correspond to the various oxidation states of transition metal ion, 4) large amount of electrochemical energy can be stored or released during the redox reaction.

In this thesis, transition metal oxides are employed as the electrode for two types of electrochemical devices to illustrate the effects of the modified oxide electrode for practical applications. The first electrochemical device is electrochromic (EC) device, which operates based on the optical properties associated with oxidation states of transition metal ion. On the other hand, the second type is the supercapacitors. Differ from the EC device, which is focusing on the optical properties, supercapacitor is focusing on the charge storage capabilities during the electrochemical reactions.

2.2.1 Electrochromic (EC) device

Figure 2.6 Schematic view of EC device ¹³

A complete EC device usually consists of four or five layers as shown in Figure 2.6, including: conductive layer → ion storage film or electrochromic (EC) material → electrolyte → electrochromic materials → conductive layer. A transparent substrate is required for the targeted optical application wavelength, thus glass or transparent polymer film PET is preferred in EC window for UV-Vis wavelength region. Similarly, the conductive layer also having the same transparent requirement. The common conductive layer is $\text{In}_2\text{O}_3:\text{Sn}$ (indium tin oxide, ITO) and $\text{SnO}_2:\text{F}$ on glass. Both conductive substrates are commercially available and usually having sheet resistance between $15\text{-}30\Omega/\square$. The two EC films in Figure 2.6 are representing the complementary electrochromic material, such as WO_3 (cathodic coloration) and NiO_2 (anodic coloration). In between the two electrodes is the ionic electrolyte, which is in contact with the EC material and contains small cation like H^+ , Li^+ , K^+ or Na^+ . The electrolyte is usually in liquid form for good wetting and ionic conductivity. However, the liquid electrolyte is hard to handle and requires additional encapsulation for device

application. Efforts in synthesizing all-solid state EC device have been carried out by applying gel or solid electrolyte.^{14, 15}

EC device possesses two kinds of operating states, namely, colouring and bleaching state. The colouring state is referring to the reduction in transmittance upon voltage biasing while the bleaching state is referring to the increase in the transmittance at the reversed voltage bias.¹³ Several types of the EC device have been designed based on the EC phenomenon. Figure 2.7 illustrates the schematic view of smart windows, reflectance mirror and emitting surface which operates based of the reflection or different degree of light wave adsorption at different voltage bias.

Figure 2.7 The principle of electrochromic devices. Arrows indicate the incoming and outgoing light wave (thickness of arrow - the light intensity, blue-colored, white-bleached).

Depending on the optical properties at reduced state (i.e. at negative voltage), the EC material can be further categorized into anodic material and cathodic material. Cathodic EC material, such as WO_3 , Ta_2O_5 , MoO_3 , Nb_2O_5 , and TiO_2 , will be coloured upon electron-ion double injection. Vice versa, the anodic EC material, such as Cr_2O_3 ,

MnO₂, FeO₂, CoO₂, NiO₂ and RhO₂ will be coloured upon electron-ion double extraction.¹³ These two categories of EC material are hence complementary to each other and can be applied on working and counter electrode in EC device (Figure 2.6) to enhance the contrast or produce different colouring effect.

As shown in Section 2.1, the interface of oxide and electrolyte is very important as it governs the reaction sites for surface reaction (including EDL and surface charge transfer reaction) and it is the starting point of the ion diffusion process. Since the optical modulation in EC device is depending on the availability of reduced or oxidized transition metal ion, various synthesis methods have been demonstrated to increase the oxide-electrolyte interface and hence the redox reaction. Two types of porous oxide layer with effective electrolyte penetration have been demonstrated for EC electrode to achieve large oxide-electrolyte interfacial area. The first type of oxide layer composed of three-dimensional interconnected network of the transition metal oxide, including the mesoporous¹⁶⁻²⁰ and macroporous²¹⁻²³ oxide layer. Template assisted synthesis has found to be an effective method in producing these porous oxide layers. The employed template can be soft template such as surfactant SDS^{16, 20, 24} and block co-polymer¹⁸ or hard template such as polystyrene (PS) spheres.^{21, 22} After removing the template through chemical dissolution or heating, the initial cavity occupied by the template becomes interconnected pores. These interconnected pores form pathways for electrolyte penetration and create more oxide-electrolyte interfaces for electrochemical reactions. These advantages associated with mesoporous or macroporous oxide layer have facilitated the ion transportation and enhance the switching kinetic, current density, optical modulation of the oxide.

The second type of porous oxide layer composed of oxide nanostructures such as 0D nanoparticles²⁵ or 1D nanorods²⁶⁻²⁸ and nanobelts²⁹⁻³¹. Large oxide-electrolyte

interfacial area can be achieved by the high surface to volume ratio in nanostructures. The nanostructures are assembled into an oxide layer with point contact or line contact while leaving interconnected pores for electrolyte penetration and wetting. Similar to the mesoporous and macroporous oxide layer, the surface of the nanostructure, which is in contact with the electrolyte, serves as the reaction site for the electrochemical reaction.

There three main EC properties which are governed by the electrochemical reactions in transition metal oxide. The first property is the optical modulation at colouring and bleaching state. In transition metal oxide, the oxide's intrinsic property determines the preferential transmittance of specific UV-Vis wavelengths and hence each oxide exhibits their unique colour. On the other hand, the colouration intensity (i.e. the degree of transmittance, which is usually presented in percent) and hence the contrast is governed by the amount of reduced or oxidized transition metal ion, and reflected as the current and the amount of charge during the reaction. However, this method is rather indirect for the optical performance judgement. A more direct evaluation on optical modulation by comparing the transmittance at colouring and bleaching state is hence employed for EC device. The transmittance level of a specific wavelength can be extracted from the transmittance spectra. The transmittance level reflects the colouration intensity while the difference in the transmittance level determines the contrast (i.e. optical modulation) of the EC device at colouring and bleaching state. In this thesis, WO_3 has been employed as the electrode material for EC device. WO_3 exhibits blue colour at colouring state and transparent at bleaching state. In other words, full transmittance for all UV-Vis wavelengths at WO_3 bleaching state and red-end light waves are strongly absorbed at colouring state. The strongest optical modulation in WO_3 occurs at the near infra-red (IR) region. Generally, the porous

oxide electrode exhibits comparable optical modulation with WO_3 bulk or thin film, which is around 70 %.^{23, 24} However, there are also some reports of porous oxide electrode^{27, 28} showing lower optical modulation, which imply that modifying the oxide into porous structure could potentially degrade the optical modulation. Hence, consideration has to be taken to avoid severe compensation in optical modulation while creating porous electrode to facilitate the redox reaction.

The second EC property is the switching time, which is controlled by reaction kinetics of the redox reaction in transition metal oxide. The optical modulation is associated with the redox reaction of the transition metal ion and the speed of the optical modulation is basically governed by how fast is the redox reaction takes place and the corresponding optical responses upon the charge insertion / extraction. Switching time is used as the indicator for the reaction kinetics of redox reaction and the corresponding optical modulation. The switching time is defined as the time required for a specific amount of optical modulation and can be further categorized into colouring time and bleaching time.^{18, 19, 27} Generally, WO_3 exhibits colouring and bleaching time ranging from several seconds up to hundreds of second.³²⁻³⁴ The redox reaction kinetic is significantly affected by the oxide morphology and dimension and tailoring WO_3 into mesoporous film or nanostructures can significantly reduce the colouring and bleaching time to less than 10 s.^{18, 19, 24, 27, 28} For example of mesoporous WO_3 film demonstrated by Wang et al., the bleaching time can be shortened to 2s while the colouring time is only 11 s.¹⁹ Similarly, Deepa et al. have demonstrated mesoporous WO_3 film (around 200 nm of WO_3 grain size) which exhibits similar colouring and bleaching time of 3 s and 2 s, respectively.²⁴ Short colouring and bleaching time are also being observed in WO_3 nanostructures. Park et al. have demonstrated WO_3 nanorods around 3 nm in diameter which exhibit excellent

colouring and bleaching time of 2.8 s and 1.6 s, respectively.²⁷ These results have clearly illustrated that modifying the oxide into porous oxide layer can significantly enhance the switching kinetic in transition metal oxide. The enhancements are attributed to the large oxide-electrolyte interface and short ion diffusion distance of the porous oxide. However, there is lack of or only very limited detail investigation on how porous oxide layer (with oxide of sub-100nm dimension) promote the electrochemical reaction and its correlation to the EC performances.

Coloration efficiency (CE) is another important criterion for EC device. The CE represents the optical density (OD) of transition metal oxide per inserted charge. CE reflects the correlation between the electrical and the optical response of the oxide electrode. High CE is required for an EC device as significant optical modulation can be achieved with only small amount of charge insertion / extraction, which implies that only a small amount of energy is required to operate the EC device. However, even for the same transition metal oxide, CE varies with different synthesis method and morphology of the oxide electrode. For example of WO_3 , CE can vary between $20 \text{ cm}^2 \text{ C}^{-1}$ to $76 \text{ cm}^2 \text{ C}^{-1}$.^{18, 19, 23-25, 28} High CE, which exceeds $90 \text{ cm}^2 \text{ C}^{-1}$, has been reported in some modified oxide electrode. CE of $90 \text{ cm}^2 \text{ C}^{-1}$ has been observed by Deepa et al. in nanostructured mesoporous WO_3 film.²⁴ Moreover, Park et al. have employed WO_3 nanorods as EC electrode and obtained high CE of $141 \text{ cm}^2 \text{ C}^{-1}$.²⁷ However, the detail mechanism of CE enhancement in these porous WO_3 layer is still unclear. Nevertheless, there are also reports of inferior CE in mesoporous WO_3 film¹⁸ and WO_3 nanostructures²⁸, which only exhibit CE of $23 \text{ cm}^2 \text{ C}^{-1}$ and $38 \text{ cm}^2 \text{ C}^{-1}$, respectively. Based on these reported results, it is clearly that there is a lack of understanding in the correlation between electrical response and optical performance for porous WO_3 layer. Inappropriate modification in oxide electrode might enhance

the switching kinetic or optical modulation but degrade the CE. Hence, further study on the porous oxide layer is required to establish the fundamentals for the enhancement in EC performance.

In summary, EC performances of the transition metal oxide can be enhance through modifying the oxide electrode into porous structure. With changing from bulk oxide into porous oxide layer, the electrochemical reactions in the oxide are altered and the EC performances can be enhanced. However, there is a lack of understanding in the enhancement mechanism and this could be the reason for some inferior EC performances after the oxide modification. Hence, systematic studies on non-porous and macroporous WO_3 have been carried out in the Chapter 4 of this thesis to demonstrate the effects of porous oxide layer on the electrochemical and EC performances and establish the fundamental principles for enhancing the performances in transition metal oxide electrode.

2.2.2 Supercapacitor

Figure 2.8 Ragone Plot for energy density and power density of energy storage devices

Figure 2.8 displays the Ragone plot of energy storage devices, which illustrates the energy density, power density and the expected charging-discharging time. The energy storage devices are located at the two ends in the Ragone plot. Fuel cell and battery are well known for high energy density application. However, the limitation in the reaction kinetic has resulted in low power density because the devices are unable to deliver the energy within short duration. In contrast, conventional electrostatic capacitor exhibits superior power density. However, the total stored energy (and hence the energy density) is limited by the small capacitance of charge separation process at the electrode-dielectric interface. Hence, a performance gap exists and supercapacitor (or ultracapacitor) is designed to fill this performance gap. As shown in Figure 2.8, supercapacitor should exhibit energy density of 0.8 to 6 W h kg⁻¹ and power density of 1000 to 5000 W kg⁻¹, which implies that the charging and

discharging of supercapacitor is targeted to be completed in 5 to 40 s. Prefix of “super” or “ultra” is added for supercapacitor because the supercapacitor is several orders higher in energy density as compared to conventional capacitor.⁵ With these unique energy storage performances, supercapacitor can be applied for electrical vehicles, consumer electronics and power management system in industrial.^{5, 35, 36}

Figure 2.9 Schematic view of (a) electrical double layer capacitor (EDLC) and (b) the charge separation in EDLC.^{3, 5}

Depending on the electrochemical reaction mechanism, the supercapacitor can be further categorized into electrical double layer capacitor (EDLC) and pseudocapacitor.⁴ EDLC stores the charge in the electrical double layer (as discussed in Section 2.1) at electrode-electrolyte interface and the cations and anions in the electrolyte are attracted to the electrode of opposite polarity upon the voltage biasing. The electrochemical energy is hence stored in the EDL (Figure 2.9). When the voltage is reversed, the cations and anions are expelled away from the electrode, recombine in the electrolyte and the energy is released. Since the energy storage only involves the charge separation and recombination at the electrode-electrolyte interface, EDLC possesses fast reaction kinetic and hence promising rate capability and power density.

^{5, 7} However, similar to the conventional electrostatic capacitor, there is only small capacitance (~ 15 to $50 \mu\text{F cm}^{-2}$) in the EDL. ³ In order to achieve the required energy density, high surface materials which have up to $500 \text{ m}^2 \text{ g}^{-1}$ or more (such as aerogel and xerogel ³, CNT ³⁷⁻⁴⁰, activated carbon ^{41, 42}, ordered mesoporous carbon⁴⁰) are employed as the electrode material of EDLC. Generally, the EDLC exhibit slightly lower specific capacitance (SC) less than 180 F g^{-1} ^{37-41, 43}, resulting in lower energy density as the SC is correlated to the energy density (E) as $E = \frac{1}{2} (\text{SC})V^2$, where V is the potential window.

Differ from the EDLC, pseudocapacitor operates based on the redox reaction, which involves charge transfer and is a Faradic reaction. Through the insertion and extraction of the charge carriers (i.e. electron and ion), the electrochemical energy is stored or released. Electrical conducting polymer (ECP) and transition metal oxide, which exhibit reversible redox reaction such as polyaniline ^{44, 45}, polythiophene ^{46, 47}, polypyrrole ^{48, 49}, RuO_2 ^{50, 51}, V_2O_5 ⁵²⁻⁵⁴ and MnO_2 ⁵⁵⁻⁵⁷, have been studied as the electrode of pseudocapacitor. All these materials operate in similar way: the active material is reduced upon the electron injection while cation is simultaneously intercalated adjacent to the reduced site. At reversed voltage bias, the active material is oxidized upon electron extraction and the ion is expelled back into the electrolyte. In general, the redox reaction can provide more charges as compared to the EDL, which is reflected by the SC of the pseudocapacitor is generally higher than EDLC. ^{19, 55, 56,}

⁵⁸⁻⁶¹ Among the electrode materials, transition metal oxides have attracted large attention for its high SC, which is beneficial in providing high energy density. However, the redox reaction in transition metal oxide possesses slower reaction kinetic as the reaction rate is limited by the slow ion diffusion. Moreover, as compared to EDLC, the stresses induced during the ion intercalation and de-

intercalation cause structural strain and shorten the electrode lifespan.⁷ Fortunately, progresses in electrode architecture have increased the cycling stability of transition metal oxide up to thousand or more cycles with only less than 20 % degradation in SC.^{36, 62-65} The promising cycling stability can elongate the lifespan of the oxide electrode, which is essential for an energy storage device. In summary, the high SC and moderate stability of the transition metal oxide are attractive for supercapacitor application and the main drawback of the oxide is the slow reaction kinetic.

Figure 2.10 Specific capacitances (SC) of potential transition metal oxide candidates for supercapacitor electrode material: RuO₂^{50, 66-69}, V₂O₅^{19, 35, 52-54}, MnO₂^{56, 57, 62, 70, 71}, Mn₃O₄^{60, 72}, Co₃O₄⁷³⁻⁷⁵, SnO₂^{76, 77}.

There are two main properties to be considered during the selection of a suitable electrode material for supercapacitor. The first criterion is the specific capacitance (SC) of the material, which reflects the charge storage ability of the material and is directly affecting the energy density of the supercapacitor. Among various transition metal oxides (Figure 2.10), RuO₂ has been reported with the highest SC ranging from

700 to 1500 F g⁻¹.^{50, 51, 66, 69, 78} However, the expensive cost of RuO₂ has limited its wide application as the electrode material.^{7, 56, 79} Hence, research efforts have been carried out on other transition metal oxides, such as Co₃O₄⁷⁵, Mn₃O₄⁶⁰, MnO₂^{55, 56, 62}, NiO^{61, 64}, SnO₂^{76, 77}, TiO₂⁸⁰ and V₂O₅^{35, 36, 81} to find the suitable replacement for RuO₂. The SC of these potential candidates are shown in Figure 2.10. Generally, the SC of these oxides are lower than RuO₂ and most of them are less than 400 F g⁻¹. However, these SC are still higher or comparable to EDLC. Hence, the transition metal oxides are promising candidates for supercapacitor if its rate capability can be significantly improved. Among the oxides, V₂O₅ has attracted large attention for its high SC up to 350 F g⁻¹⁵³ and has been selected as the material of choice in this thesis. The layered structure of V₂O₅ provides flexibility for oxide modification^{2, 82} as it allows atomic level modification such as metal doping and lattice structure alteration, which are attractive for further enhancement in the electrochemical reaction and charge storage performances.

The second property is the rate capability. The rate capability governs the power density of the supercapacitor. There are two main aspects for the rate capability: the SC at high charging-discharging rate and the SC retention across the increasing rate. These two terms reflect the charge storage capability of the material at high charging-discharging rate, as the supercapacitor is designed for high power application. The rate capability in transition metal oxide is a challenge because the reaction is limited by the slow ion diffusion in the diffusion controlled redox reaction.¹ The inferior rate capability reduces the power density and limits the supercapacitor application. As shown in Section 2.1, the redox reaction at the oxide-electrolyte surface exhibits capacitive response and possesses much faster reaction kinetic as compared to the diffusion controlled redox reaction.^{1, 6, 55} Hence, the rate capability of the transition

metal oxide can be improved if this surface redox reaction is largely promoted and dominates the overall reaction.

In short, transition metal oxides exhibit superior SC for supercapacitor application but are limited by the slow ion diffusion process during the electrochemical reaction. Rate capability of transition metal oxides needs to be improved to achieve high energy density and high power density. Based on the reaction mechanism, systematic study on the oxide electrode modifications have been designed and studied in this thesis to provide fundamental understandings for further improvement in the oxide electrode performance.

2.3 Summary

In Section 2.2, the state of art and challenges of electrochromic (EC) device and supercapacitor have been reviewed. The basic reaction which governs the device performance (i.e. optical properties and charge storage) in transition metal oxide is the redox reaction and the main limitation is the slow reaction kinetic of the redox reaction. Hence, the oxide electrode should be specially tailored to facilitate the reaction to achieve fast reaction rate and enhance the rate capability. Moreover, the redox reaction should also be simultaneously promoted to increase the total stored charge and the capacitance. In this thesis, several oxide modifications are designed based on the reaction mechanism to achieve these two goals. As shown in Section 2.1, the redox reaction can be further categorized into surface charge transfer process and diffusion controlled reaction. The surface charge transfer reaction takes place at the oxide-electrolyte interface with capacitive response. On the other hand, the diffusion controlled reaction is the rate limiting step and requires solid state ion diffusion before the ion is intercalated adjacent to the reduced transition metal ion. Based on these understanding, we design modifications on oxide electrode with the aim of 1) increasing the redox reaction (hence the charge contributed by the reaction) and 2) enhancing the rate capability.

The first aspect to be considered is the oxide-electrolyte interfacial area, which is the reaction site for surface dependent reactions (including the EDL and surface charge transfer reaction) and the starting point of the diffusion controlled reaction. In bulk transition metal oxide, the oxide-electrolyte interfacial area is only the oxide surface area which is in contact with the electrolyte. Hence, the charge contribution from the surface dependent reaction is negligible and rate capability is unsatisfactory as the overall reaction is dominated by the slow diffusion controlled redox reaction. Hence,

the main targets are to promote the fast surface dependent reaction to improve the reaction kinetic and increase or maintain the high capacitance of transition metal oxide. These can be achieved through increasing the oxide-electrolyte interface. The total capacitance can hence be increased by the additional charge contribution from the surface dependent reaction with the increase in reaction site. Moreover, the rate capability of the oxide can be improved as the overall reaction is less dominated by the slow diffusion reaction.¹

As mentioned in previous sections, ion diffusion process is the main limiting step of the redox reaction in transition metal oxide. In order to achieve promising rate capability, short diffusion time is required and it can be achieved by shortening the ion diffusion distance or creating fast diffusion pathway. The ion diffusion distance can be significantly reduced by employing oxide layer composed of nanometer scale oxide as the working electrode. In another word, the whole oxide layer can be activated within short time as most of the ion diffusion distance has been replaced by the electrolyte penetration. Similar principle works for the extraction of ions from the oxide during oxidation: the ions can be expelled back to the electrolyte within short duration as the ions are not required to diffuse across the whole oxide layer. This will reduce the diffusion time and hence further improve the rate capability. Diffusion pathway is another essential criterion which affects the diffusion process. Ion diffusion takes place in the oxide lattice under the driving force from electric field and the ion concentration difference across the oxide layer. Through selecting an oxide with fast diffusion pathway in the lattice, the “speed” of the ion diffusion can be enhanced and the diffusion time can be shortened.

On the other hand, the transportation of electrons is another important criterion as a complete redox reaction in transition metal oxide requires the presence of both ion

and electron. However, the semi-conductive nature of transition metal oxide has limited the charge transfer rate and hence the rate capability and power density of the oxide. Hence, improving the electronic conductivity of the oxide is one of the promising routes to enhance the electrochemical performances of the oxide.⁸³⁻⁸⁵ Higher electronic conductivity can result in better charge transfer rate, promote all the electrochemical reactions (including EDL, surface charge transfer reaction and diffusion controlled reaction) in the oxide and hence enhancing the capacitance and rate capability.

The last consideration is regarding the accommodation of the charge carriers in the oxide lattice. When electrons are injected into the oxide, the cations in the electrolyte will be attracted toward the negatively charge oxide electrode, injected into the oxide and diffuse to the reduced transition metal ion. The injected electron attaches to the empty orbital of the transition metal ion and reduces it. On the other hand, the cation is accommodated at the available vacancy adjacent to the reduced metal ion to maintain charge neutrality. Hence, the properties of ion intercalation site in the oxide lattice are crucial as the redox reaction is incomplete without ion. The size and quantity of the intercalation site are significantly affects the chemisorption of solvated ions at near surface region (surface charge transfer reaction) and the intercalation process in oxide lattice (diffusion controlled reaction). The presence of easy accessible intercalation site can increase the total charge stored per unit time. In another word, the capacitance and rate capability of the oxide can both be improved.

In summary, the major challenge in the transition metal oxide is the slow reaction kinetics of the electrochemical redox reaction. This slow kinetics limit the performances of the electrochemical device, especially those concerning reaction rates, such as the switching time of the electrochromic (EC) device and rate capability of

supercapacitor. It has been found that the electrochemical performances can be significantly improved through modifying the oxides, such as tailoring the oxide morphology, lattice structure or creating fast charge transfer pathways (for ions and electrons) within the oxide. However, most reports only emphasize the performance attainable and lack detail investigation on the enhancement mechanisms related to the oxides modification. Five key electrochemical reaction factors are proposed for investigation in this thesis as summarized in Table 2.1. Through modification of the oxide nanostructures, the changes in the electrochemical reaction factors can be correlated to the improvement in performances and the enhancement mechanism can be elucidated.

Table 2.1 The key parameters of the oxide and the corresponding electrochemical reaction

Parameters	Electrochemical reaction
1) Oxide-electrolyte interface	Surface dependent reaction (EDL and surface charge transfer reaction)
2) Ion diffusion distance	Diffusion controlled redox reaction
3) Electronic conductivity	EDL, surface charge transfer reaction and diffusion controlled redox reaction
4) Diffusion pathway	Diffusion controlled redox reaction
5) Ion intercalation site	Surface charge transfer reaction and diffusion controlled redox reaction

Chapter 3 Methodology

As discussed in Chapter 2, modifications have to be carried out on transition metal oxide to enhance the reaction rate and increase the amount of redox reaction (per unit mass of material). Three strategies or approaches are designed to alter the key parameters of electrochemical reactions and their correlations are summarized in Figure 3.1.

Figure 3.1 Correlation between the oxide modification, demonstrated application and target key parameters of electrochemical reactions in transition metal oxide.

3.1 Synthesis of mesoporous WO₃ film

Non-porous and macroporous WO₃ films were synthesized through electrodeposition on bare and template coated substrate, respectively. The electrolyte for electrodeposition was prepared by dissolving 6.5 g of tungsten powder (Praxair Technologies, Al-1061) in 40 mL of H₂O₂ (Merck, 30 %) and 4 mL of de-ionized water. This oxidation of tungsten is an exothermic process and was conducted in ice bath with the temperature being controlled between 0 °C to 10 °C. Peroxy-tungstic acid (PTA) was obtained (yellow solution) after the complete dissolution of tungsten powder in H₂O₂. The PTA was filtered to remove the WO₃ precipitate and mixed with the same volume of ethanol to reduce the decomposition rate of peroxy-tungstate complex into WO₃ powder. The PTA was stored below 10 °C until the electrodeposition to further reduce the decomposition rate of peroxy-tungstate complex. The pH value of PTA was 0.6 during the electrodeposition.

Polystyrene (PS) microspheres were coated onto the substrate as the template to form macroporous WO₃ film. The PS microspheres were fabricated through emulsion polymerization. The styrene monomer was polymerized by free radical chain-growth polymerization with potassium persulphate (KPS, K₂P₂O₈) as the initiator in producing free radical.⁸⁶ The resultant PS microspheres were dispersed in de-ionized water and drop-casted onto the substrate. The PS coated substrate was overnight air-dried and annealed at 100 °C for 1 minute before the electrodeposition.

ITO coated glass (Delta Technologies, 15-25 Ω) was employed as the substrate for electrodeposition and electrochromic studies because the transparency of ITO glass allows the transmission of UV-Visible range wavelength. The ITO glass was ultrasonically cleaned in acetone, isopropanol (IPA) and de-ionized water in prior to

the PS coating or electrodeposition. The electrodeposition of WO₃ was carried out in a three-electrode electrochemical cell using potentiostat (Autolab, PGSTAT 302). Bare or PS coated ITO glass was employed as the working electrode for the electrodeposition of non-porous and macroporous WO₃ film, respectively. The counter electrode was Pt sheet while the reference electrode is Ag/AgCl. The electrodeposition was carried out at -0.45 V (vs. Ag/AgCl) at room temperature with same deposition duration of 200s for both non-porous and macroporous WO₃ film to achieve the same film thickness. The formation of WO₃ can be expressed as the reduction of peroxy-tungstate complex: ⁸⁷

The electrodeposited WO₃ films were air-dried overnight under room condition. The PS removal was carried out through immersing the electrodeposited WO₃ film in toluene. The porosity of macroporous WO₃ film was determined by comparing the density of non-porous and macroporous WO₃ film. The porosity of macroporous WO₃ film was found to be around 40 % by comparing the density of non-porous and macroporous WO₃ film, which corresponds to surface area around 2.8 m² g⁻¹.

3.2 Synthesis of un-doped V₂O₅ nanobelts

Un-doped V₂O₅ nanobelts were synthesized through hydrothermal process. 300 mg of NH₄VO₃ (Aldrich) was dissolved in 30 mL of de-ionized water and forming a clear yellow solution. The solution was adjusted to pH 2 by adding 1.0 M HNO₃ and the solution turned orange color. The resultant solution was then transferred to a Teflon-lined stainless steel autoclave and kept in an oven at 120 °C for 16 hours. Brown

precipitates were formed after the hydrothermal process, the precipitates was centrifuged and washed with de-ionized water for several times to remove the residual chemicals. The precipitates were dispersed in 30 mL de-ionized water before drop casting onto the substrate for further studies.

3.3 Synthesis of Ag doped V₂O₅ nanobelts

Ag doped V₂O₅ nanobelts were prepared via hydrothermal process. 96 mg of NH₄VO₃ (Aldrich) was dissolved in 20 mL of de-ionized water. The solution was adjusted to pH 4 by adding 1.0 M HNO₃ and followed by the addition of 23mg AgNO₃ (Aldrich). The solution was then transferred to a Teflon-lined stainless steel autoclave and kept in an oven at 120 °C or 150 °C for 16 hours to produce nanobelts with different width. The resultant brown color precipitates were centrifuged and washed with de-ionized water for several times to remove any residual chemicals. The precipitates were then dispersed in 30mL of de-ionized water and drop casted onto the substrate for further studies.

3.4 Synthesis of Na doped V₂O₅ nanobelts

Na doped V₂O₅ nanobelts were synthesized through hydrothermal process. 234mg of NH₄VO₃ (Aldrich) and 478 mg of NaCl (Aldrich) were dissolved in 20 ml de-ionized water and stirred for 1 hour until all salts were dissolved and the solution became clear yellow. The solution was adjusted to pH 4 using 3 M HCl and then transferred to a Teflon-lined stainless steel autoclave and kept in an oven at 180 °C for 24 hours. Brown colour precipitates were produced and centrifuged in de-ionized water for 6 to

8 times to remove the chemical residual. The precipitates were dispersed in de-ionized water and drop casted to the substrate. Two types of Na doped nanobelts sample were prepared: the as-synthesized nanobelts and the annealed nanobelts (air annealed at 300°C for 16 hours), which correspond to layered and framework lattice structure nanobelts, respectively.

3.5 Structural characterization

The morphology and dimension of oxides were characterized through transmission electron microscope (TEM, JEOL 2100) at an acceleration voltage of 200kV and field emission scanning electron microscope (FESEM, JEOL 7600F) to identify the ion diffusion distance in the oxide. Energy dispersive X-ray (EDX) patterns of the nanobelts were obtained through FESEM.. Powder X-ray diffraction (XRD) patterns of the oxides were collected with Bruker diffractometer using Cu K α ($\lambda=1.5418\text{\AA}$) radiation in 2θ ranging from 5 ° to 70 ° to study the crystallinity and phases of the oxide. Thermal gravitational analysis (TGA) of the nanobelts was carried out through TA Q500 in N₂ environment at 10 °C min⁻¹ heating rate. TGA was employed to investigate the weight loss of the oxide at elevated temperature, study the water content in the oxide and determine the annealing temperature of the Na doped V₂O₅. X-ray photoelectron spectra (XPS) of the 150 °C synthesized nanobelts are collected to investigate the chemical composition and oxidation states of the elements in the oxide. The XPS spectra were recorded on Kratos Analytical AXIS HSi, using Al K α radiation (1486.6eV) as the exciting source. The spectra were calibrated to C 1s peak (248.8eV). Electronic conductivity of the oxide was studied through four-point probe technique to provide information on the electron transportation in oxide lattice.

3.6 Electrochemical studies

Figure 3.1 illustrates the electrochemical cell setup for the electrochemical studies. Transition metal oxides were tested in a three-electrode cell using Autolab PGSTAT 302 with oxide / ITO glass as working electrode, Ag/AgCl as reference electrode and Pt sheet as counter electrode. The electrolyte was 1.0 M LiClO₄ in propylene carbonate (PC). Cyclic voltammetry was carried out for ± 0.5 V (vs. Ag/AgCl) with the scan rate ranging from 5 mV s⁻¹ to 100 mV s⁻¹ to investigate the I-V responses of the oxide electrode before and after the oxide modifications. Rate capability of the oxide electrode was evaluated through CV studies at scan rate ranging from 5 mV s⁻¹ to 100 mV s⁻¹. Potentiostatic Intermittent Titration Technique (PITT) study was employed to study the ion diffusion process within oxide lattice and extract the ion diffusion coefficient for comparison. PITT was carried out in the same three-electrode electrochemical cell using Autolab PGSTAT 302. The current-time (I-t) responses were recorded between -0.15 V to -0.35 V with -50 mV/step and 600 s relaxation for each step.

3.7 Optical studies

UV-Vis was carried out to study the colour and optical modulation of non-porous and macroporous WO₃ film at bleaching and colouring state in UV-Visible wavelength region. UV-Vis transmittance spectra were recorded using a UV-Vis spectrometer (Shimadzu UV-2501PC) from 300 nm to 900 nm with respect to the electrolyte. Switching time study was carried out to evaluate the switching kinetics of the WO₃

films and extract the colouring and bleaching time. The switching time characteristics between the colouring and bleaching states were extracted from the transmittance spectra at 632.8 nm using a UV-Vis spectrometer (Shimadzu UV-2501PC), while a square wave potential of ± 2.5 V was supplied from a potentiostat (Autolab PGSTAT 302). The bleaching (t_b) and colouring (t_c) time were defined as the time required for 70% transmittance modulation. Coloration efficiency (CE) of the oxide samples were calculated based on the variation in optical density (OD) upon the inserted charge.

Chapter 4 Morphology effects on electrochemical reactions and electrochromic (EC) performances in transition metal oxide

4.1 Introduction

As discussed in Section 2.2, transition metal oxides have been utilized as the electrode of electrochromic (EC) device for its electrochromism. At different oxidation states, some transition metal oxides can exhibit selective transmittance in UV-Vis wavelength region (400 nm – 700 nm). The colour and colour intensity of the oxides can be modulated by controlling the relative ratio between the metal ions of different oxidation state. Moreover, the redox reaction and hence the colour change is reversible. This allows us to design EC device to provide controllable optical modulation through manipulating the applied voltage on the transition metal oxide.^{13,}

88

Among various transition metal oxides, tungsten oxide (WO₃) has been widely studied for its unique optical modulation between transparent and blue colour.^{13, 89, 90} Moreover, EC devices, which utilizing WO₃ as the working electrode, are also available in the market, such as EC window that can be adjusted between blue colour and transparent^{88, 91} and anti-glare rear window in automobile. The electrochemical reaction in these EC devices can be expressed as:

where M⁺ represents the cations, such as H⁺, Li⁺, K⁺ and Na⁺ and x represents the amount of partial reduced W⁶⁺ and the intercalated level of M⁺.

Figure 4.1 (a) Cation intercalation at coloration state, (b) cation de-intercalation at bleaching state, (c) octahedral intercalation site in WO_3 .

The as-synthesized WO_3 film is initially transparent. When a negative voltage is applied, the electrons are injected into the WO_3 and reduce the W^{6+} into W^{5+} . In order to maintain the charge neutrality, cations in the electrolyte are attracted and injected into the WO_3 lattice (Figure 4.1a). The cations diffuse across the oxide lattice and

intercalated adjacent to the injected electrons. These W^{5+} act as the coloration centre with the whole oxide turning into blue colour. This process is referred as “coloration”. When positive voltage is applied to the oxide, electrons are extracted through the ITO glass while cations are expelled back into the electrolyte (Figure 4.1b). The W^{5+} is oxidized into W^{6+} and the oxide becomes transparent again. This process is named as “bleaching”. The coloration and bleaching are depending on the amount of W^{5+} , which is equal to the amount of electron and intercalated cation during the voltage biasing. In another word, the electrochemical and EC behaviour of the WO_3 can be studied through evaluating the current-voltage (I-V) and total charge stored in the WO_3 . As shown in figure 4.1a and 4.1b, the oxide-electrolyte interface acts as the reaction site for ion injection or extraction. The interface is crucial as the charge transfer of the redox reaction requires the participation of the cation. Hence, oxide morphology with large oxide-electrolyte interfacial area will be beneficial as the ion movement across the interface is facilitated.

From the equation 4.1, we know that a complete redox reaction in WO_3 requires the transportation of two types of charge carrier: the electron and cation. Hence, the electronic conductivity and ionic conductivity of WO_3 will directly affect the electrochemical and EC performance. However, same as other transition metal oxides, WO_3 is a semiconductor with only moderate electronic conductivity. This has resulted in slow charge transfer rate during the redox reaction and caused a long switching time required for optical modulation. On the other hand, the cation intercalation and de-intercalation are diffusion controlled processes. WO_3 possesses a three dimensional framework structure composed of WO_6 octahedron and the cation can be intercalated at the octahedron intercalation sites (as shown in Figure 4.1c). During the

redox reaction, the cation needs to diffuse for a distance between the intercalation site and the oxide-electrolyte interface, which is also called as the ionic diffusion distance. In WO_3 , the diffusion coefficient is typically around $10^{-10} \text{ cm}^2 \text{ s}^{-1}$ to $10^{-11} \text{ cm}^2 \text{ s}^{-1}$.^{92, 93} Long diffusion time is hence required in bulk WO_3 due to the long ionic diffusion distance between the oxide-electrolyte interface and the inner part of the oxide. This would result in slow response in an EC device.

Considering the issues of the charge carrier movement across the interface and within the oxide, a facile method of improving the charge carrier transportation and charge transfer rate by tailoring the WO_3 morphology and dimension is demonstrated in this chapter. WO_3 is tailored into macroporous structure through template assisted electrodeposition. The connected pores within the macroporous WO_3 allows the electrolyte penetration into the inner part of the oxide layer. This brings two benefits: more oxide-electrolyte interface is created and the ionic diffusion distance is reduced from the oxide layer thickness down to the wall thickness (between the adjacent pores). With more oxide-electrolyte interface, more charge transfer and ion injection across the interface can occur per unit time and per unit volume of material. This can increase the overall charge transfer rate and compensate disadvantages from the low electronic conductivity. In addition, although the diffusion coefficient of cation is low, the short ionic diffusion distance can shorten the diffusion time and enhance the overall reaction kinetics. Coupling the advantages from these two aspects, WO_3 can be designed into a more promising electrode for EC application with enhanced reaction kinetic, switching properties and coloration efficiency.

In this chapter, the macroporous and non-porous WO_3 with same thickness are compared to evaluate the enhancements in electrochemical and EC performances. Electrochemical redox reaction, charge intercalation, optical modulation and optical

switching are studied to provide further understanding on the effects associated with different oxide morphology. Further discussion on the optical and electrical response, solid state ion diffusion and ion intercalation are also presented in this chapter. These studies serve as a directive strategy in designing promising transition metal oxide electrode for EC or electrochemical application.

4.2 Structural Characterization of non-porous and macroporous oxide film

Figure 4.2 (a) Schematic view of WO_3 electrodeposition with and without polystyrene (PS) template, (b) FESEM image of the PS template on the ITO substrate [Inset: the diameter distribution of PS spheres], (c) macroporous WO_3 film after PS removal in toluene, (d) non-porous WO_3 film.

Figure 4.2a demonstrates the schematic view of template assisted electrodeposition of WO_3 . ITO coated glass was selected as the substrate due to its transparency at the UV-Vis wavelength, which is essential for EC application. Polystyrene (PS) spheres were coated onto the ITO glass in prior of the immersion of the coated substrate in the

electrolyte. Figure 4.2b shows the FESEM image of PS spheres coated ITO glass. The histogram of the PS sphere diameter is shown as the inset in Figure 4.2b where the PS spheres have a mean diameter of 235 nm. The PS coated substrate is immersed in the electrolyte of peroxy-tungstate acid, which contains peroxy-tungstate complex $[W_2O_{11}]^{2-}$ or $[(O)W(O_2)_2(O)(O_2)_2W(O)]^{2-}$, where (O_2) denotes a peroxide ligand.⁸⁷

During the electrodeposition, the electrolyte infiltrates into the cavities among the PS spheres. When the voltage is applied onto the ITO glass, the peroxy-tungstate complex is broke down and reduced as:⁸⁷

WO_3 was precipitated and filling the cavities among the PS spheres. After the electrodeposition, the electrodeposited film was immersed in the toluene to dissolve the PS spheres. Figure 4.2c shows the FESEM image of the macroporous WO_3 film after the PS spheres removal. The pore diameter is around 235 nm, which corresponds to the mean diameter of the PS spheres. Interconnected pathways can be found between the adjacent pores, which are very important as the ionic electrolyte can penetrate into the inner part of WO_3 through these pathways. The cation in the electrolyte is hence “delivered” into the inner part of the oxide layer. The wall thickness in macroporous WO_3 (between two adjacent pores) is around 100nm and both sides of the wall can act as the reaction site for cation injection or extraction during redox reaction. Non-templated ITO glass was used as the substrate to synthesize non-porous WO_3 film for comparison (Figure 4.2a). Same deposition duration is applied for the electrodeposition of macroporous and nonporous WO_3 film to achieve same film thickness of 600 nm. Through calculating the densities of macroporous and nonporous WO_3 film, the porosity of the macroporous WO_3 film is

found to be around 40 %. Figure 4.2d shows the FESEM image of the non-porous WO₃ film.

4.3 Studies of redox reaction and charge intercalation in macroporous and non-porous oxide film

Figure 4.3 Cyclic voltammograms of the macroporous and non-porous WO₃ film at 100 mV s⁻¹ scan rate. (Electrolyte: 1 M LiClO₄/PC)

Cyclic voltammetry (CV) was carried out on macroporous and non-porous WO₃ film to investigate the current-voltage (I-V) response in WO₃ during the electrochemical redox reaction. Both WO₃ films were cycled between ± 1.0 V (vs. Ag/AgCl) in 1.0 M Li⁺ electrolyte (LiClO₄ in propylene carbonate) at 100 mV s⁻¹ scan rate. Figure 4.3 displays the cyclic voltammograms of non-porous and macroporous WO₃ film. Both samples exhibit a similar CV curve feature, which suggests that similar redox reaction

occurs within both samples under the voltage cycling. The reduction peak occurs at -1.0 V while the oxidation peak locates around -0.6 V. Similar features have also been reported for WO₃ EC devices.^{25, 34, 94} The current in the CV curves have been normalized to the mass of the WO₃ to study the current densities in macroporous and non-porous WO₃ film. The macroporous WO₃ film exhibits larger current density as compared to the non-porous WO₃ film. This suggests that within unit time (or under same scan rate), the macroporous WO₃ film has a higher charge transfer rate and more redox reactions occur as compared to non-porous film. Similar observations have been reported in porous WO₃ film.^{95, 96} The area under the CV curve represents the total charge stored in the WO₃. As shown in equation 4.1, the total stored charge (i.e. the total amount of electrons) is equal to amount of intercalated cation. Hence, the cation intercalation level can be determined based on the total stored charge. The non-porous WO₃ film possesses total stored charge of 3.5 C g⁻¹, which corresponds to 0.008 Li⁺ per WO₃. In contrast, the macroporous WO₃ film possesses larger area under CV curve and can accommodate up to 5.6 C g⁻¹, which corresponds to 0.013 Li⁺ per WO₃ and is 1.6 times higher than the non-porous WO₃ film. Since there is no additional redox peaks or significant changing in the redox peak position in the macroporous film, this increment in the total stored charge and Li⁺ intercalation level are not due to any different or additional redox reaction. The enhancements should be attributed to the advantages associated with the macroporous structure, where the redox reaction has been facilitated by having more oxide-electrolyte interface and short ionic diffusion distance. Both advantages can enhance the charge transfer rate by creating more reaction sites and shorten the diffusion time of Li⁺. In this case, more redox reactions can occur within unit time and larger current density is hence achieved in the macroporous WO₃ film. In another word, the macroporous WO₃ film

is more efficient in the charge transfer as compared to the non-porous WO_3 film, which is expected to enhance the optical performances as the coloration and bleaching process are directly related to the redox reaction.

4.4 Studies of optical modulation and colour switching in macroporous and non-porous oxide film

Figure 4.4 UV-Vis transmittance spectra of the (a) non-porous and (b) macroporous WO_3 film at coloration and bleaching state.

Figure 4.4 presents the transmittance spectra of the non-porous and macroporous WO_3 film with the WO_3/ITO glass acts as the working electrode and a Pt wire acts as the reference electrode and counter electrode. Both samples are coloured at -2.5 V and bleach at $+2.5$ V for 200 s. The transmittance spectra for wavelength ranging from 300 nm to 900 nm are simultaneously recorded. Similar features in the coloration and bleaching transmittance spectra are observed in both samples. During the coloration, electrons are injected into the WO_3 film and partially reduce from W^{6+} to W^{5+} . When the light is subjected onto WO_3 film, red-end light waves are adsorbed and only blue-

end light waves can pass through the film. The transmittance spectrum at coloration state hence exhibits a transmittance peak around 400 nm and low transmittance at the red-end light wave around 700 nm, which results in the blue colour observation during coloration. On the other hand, the electrons are extracted and the W^{5+} is oxidized back to W^{6+} during the bleaching state. The light wave in UV-Vis region can transmit through the WO_3 film and the film become transparent. The light wave transmittance at the bleaching state is nearly a constant value at the UV-Vis region. Both macroporous and non-porous WO_3 film possess a transmittance around 80 % - 90 % at the bleaching state. On the other hand, the transmittances of the two samples at coloration states are very different. The transmittance peak of non-porous WO_3 film is located around 375nm. In contrast, the transmittance peak of macroporous WO_3 film is broadened and exhibits high transmittance for the wavelength between 375 nm to 525 nm. This difference in the peak shape and location can be attributed to the interference of light wave in the macroporous film. Consider the light wave travels from one medium: a spherical cavity which filled with the electrolyte ($LiClO_4$ in propylene carbonate) to another medium: WO_3 . Destructive and constructive interference will occur if the travel distance, t , (i.e. the distance travelled in the pores) fulfills the criterion $t=1/2m\lambda$ or $t=1/2(m + 1/2)\lambda$, respectively. Since the pore in macroporous film is around 235 nm in diameter (Figure 4.2), destructive interference is likely to occur for the wavelength between 350 nm to 470 nm, which corresponds to the pore diameter of 175 nm to 235 nm (Table 4.1). Hence, the transmittance between 350 nm to 470 nm wavelength is decreased and the transmittance peak is broadened and centralized around 470 nm for the macroporous film.

Table 4.1 Destructive and constructive interference for wavelength between 350 nm to 500 nm and the corresponding travel distance in the pore.

Wavelength (nm)	Travel distance t (nm)	
	Destructive interference	Constructive interference
350	175.0	262.5
400	200.0	300.0
425	212.5	318.8
470	235.0	352.5
500	250.0	375.0

The difference between the transmittance at bleaching and coloration state at a fixed wavelength is defined as optical modulation ($\Delta T\%$). In this work, the optical modulations are extracted at 700 nm, which is the largest optical modulation within the UV-Vis region. The non-porous WO_3 film possesses an optical modulation of 88 %. In contrast, the macroporous WO_3 film exhibits a lower optical modulation of 38 %. The results have signified a disadvantage of macroporous film: for the same thickness of oxide layer, the porosity in macroporous structure leads to less active material for coloration and results in smaller optical modulation. For the application which requires deep colour or significant contrast between coloration and bleaching, thicker oxide layer is required to compensate the effect of porosity in macroporous film.

Step voltage has been applied to the non-porous and macroporous WO_3 film to simulate the switching condition in EC devices. The films are coloured at -2.5 V and bleached at $+2.5$ V (Figure 4.5a). Figure 4.5b and 4.5c display the transmittance spectra of the macroporous and non-porous WO_3 film at coloration and bleaching

state. Each voltage is hold for 200 s and the corresponding transmittance (at 633 nm) is recorded. The switching time between coloration and bleaching step is defined as the time required for a fixed amount of optical modulation (ΔT %). In this work, the switching times for 70 % of the total optical modulation (ΔT %) is evaluated to compare with the reported results in the literatures. For non-porous film, the coloration time is 11.2 s and the bleaching time is 5.3 s. This value is comparable to the WO_3 thin film synthesized through sol-gel^{33, 34} and electrodeposition³² (coloration time: 30 - 94 s, bleaching time: 5 - 30 s). In contrast, the coloration and bleaching time in macroporous film are 7.7 s and 2.1 s, respectively. This is around 50 % faster than the non-porous film. The switching time in the macroporous film is better as compared to the reported mesoporous film (coloration time: 8.9 - 20 s, bleaching time: 4.5 - 15 s)^{24, 97} and macroporous film (coloration and bleaching time ~ 8 s).⁹⁸ The results clearly indicate the enhancement in the redox reaction kinetic and optical response after tailoring the WO_3 into macroporous structure. As discussed in Section 4.3, the charge transfer rate of the redox reaction has been improved in macroporous film and more redox reaction can occur in unit time. In another word, in order to achieve the same amount of coloration centre (W^{5+}) and coloration intensity, shorter time is required in macroporous film. This has greatly improved the efficiency of the EC device as the coloration and bleaching process can be completed within a short duration.

Figure 4.5 (a) Step voltage of ± 2.5 V applied on WO₃ films, transmittance spectra of the (b) non-porous and (c) macroporous WO₃ film at coloration and bleaching state (at 633 nm).

4.5 Effects of oxide morphology on optical and electrical responses

Figure 4.6 The plot of normalized transmittance vs. current for (a) non-porous and (b) macroporous WO₃ film during coloration.

Figure 4.6 presents the correlation between the transmittance and current in the non-porous and macroporous WO₃ film. In the earlier discussions, the correlation between electrical signal (i.e. the amount of electron and intercalated cation) and the optical modulation is simplified as W⁵⁺ is responsible for the optical modulation and the W⁵⁺ is instantaneously formed upon inserted electron (i.e. current flow). In this ideal situation, the transmittance and current should vary in phase and follow the dotted straight line in Figure 4.6. In real EC electrode, the change in the transmittance is found to be lagging behind the current and the curve deviates from the dotted straight line. This is an issue where the colour change in the EC device is not “instant” as there is a time lag in the optical response of the device after applying the switching voltage. Through tailoring the WO₃ into macroporous structure, the response in

optical modulation upon the current has been significantly improved as the curve is closer to the ideal dotted line. Moreover, for the same amount of intercalated charges, the macroporous structure is generally exhibiting larger optical modulation. These results suggest that macroporous film is a more efficient EC electrode for optical modulation.

In order to quantify the efficiency of coloration in an EC electrode, the coloration efficiency (CE) is used. CE signifies the correlation between optical and electrical response. A promising EC electrode should exhibit a high CE, where significant optical modulation can be achieved with only small amount of intercalated charges. The CE ($\text{cm}^2 \text{C}^{-1}$) is defined as the variation in optical density (OD) per unit of intercalated charges:⁹⁹

$$CE = \frac{\Delta OD}{\Delta Q} = \frac{\log(T_{\text{bleach}}/T_{\text{color}})}{q/A} \quad (4.3)$$

where T_{bleach} and T_{color} represent the transmittance at bleaching and coloration state, respectively. Q is the charge density (C cm^{-2}), which equals to the total charge q (C) per unit electrode surface area A (cm^{-2}). Optical densities (OD) of the non-porous and macroporous WO_3 film are plotted against the intercalated charges in Figure 4.7.

Figure 4.7 Charge density dependence of optical density (OD) of (a) non-porous and (b) macroporous WO₃ film. The coloration efficiency (CE) is evaluated from the linear region of the curve.

The CE of each sample can be extracted from the slope at the linear dependence region in the figure. The non-porous WO₃ film possesses CE of 55 cm² C⁻¹. This value is higher than the crystalline WO₃ nanostructures (CE of 42 cm² C⁻¹)²⁵ and comparable to the reported macroporous WO₃ film (CE of 58 cm² C⁻¹)⁹⁸ and nanostructured WO₃ film (CE of 60 cm² C⁻¹)¹⁰⁰. On the other hand, the CE in the macroporous film in this work is significantly increased up to a CE of 90 cm² C⁻¹, which is almost double that of the non-porous film CE. This value is higher than the

general reported CE value ($60-70 \text{ cm}^2 \text{ C}^{-1}$) of mesoporous WO_3 .^{24, 97} The results further support the observation in the step voltage study (Section 4.3), where the reaction kinetic has been greatly improved in the macroporous structure and leads to higher efficiency in coloration. Beyond the linear region, the OD is nearly a constant value and independent of the intercalated charge for both samples. This can be explained by the considering the coloration mechanism in WO_3 . A site saturation model for optical efficiency (i.e. CE in EC device) has been previously reported by Denesuk et. al..¹⁰¹ The coloration in transition metal oxide is due to the light wave adsorption and localized electrons transfer to the available empty sites adjacent to the reduced metal ion. With the increase in the intercalation level (i.e. the charge density), these empty sites are occupied (i.e. the site saturation) and hence only small level of optical modulation can be observed. Hence, the OD for both macroporous and non-porous WO_3 film is nearly a constant value at high intercalation level.

4.6 Effects of oxide morphology on solid state ion diffusion in oxide lattice

A complete redox reaction in WO_3 involves the cation injection / extraction across the oxide-electrolyte interface and solid state diffusion. However, the slow diffusion has limited the overall reaction kinetic, which resulted in the slow response and long reaction time in WO_3 . This problem can be encountered through improving the cation diffusion coefficient or reducing the ionic diffusion distance. The diffusion time of the cation can be express as:

$$t = \frac{l^2}{D} \quad (4.3)$$

where t stands for diffusion time (s), l is the ionic diffusion distance (cm) and D is the diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$). The increase in the diffusion coefficient is similar to the cation possesses a “faster speed”, which helps to reduce the diffusion time. On the other hand, shortening the ionic diffusion distance also helps to reduce the diffusion time, especially the diffusion time is proportional to the square of the diffusion distance. In previous sections, enhancements in the total stored charge, switching time and coloration efficiency (CE) have been observed in the macroporous WO_3 film. These enhancements could possibly due to the shortening in the ionic diffusion distance or the improved diffusion coefficient in the macroporous structure or both.

FESEM image of the macroporous structure provides the information regarding the ionic diffusion distance. As shown in Figure 4.2c, the wall thickness between the adjacent pores is around 100 nm. Considering the electrolyte has penetrated into the pores, both sides of the wall are now oxide-electrolyte interface. The cations can be injected from both sides of the wall and hence the ionic diffusion distance should be half of the wall thickness, i.e. around 50 nm. As compared to the non-porous film,

which is 600 nm in thickness, the ionic diffusion distance in the macroporous structure is 12 times smaller.

Potentiostatic intermittent titration technique (PITT) has been carried out to investigate the diffusion coefficient in the non-porous and macroporous WO₃ film. The study was carried out in 1 M LiClO₄ /PC electrolyte with four voltage step (-50 mV per step) ranging from -0.15 V to -0.35 V (vs. Ag/AgCl) and 600 s relaxation time for each step. The diffusion coefficient can be determined through the following expression at the Cottrell region (time independent region):¹⁰²

$$\frac{Q(t)}{\sqrt{t}} = \frac{2\sqrt{D}\Delta Q}{l\sqrt{\pi}} \quad (4.4)$$

where $Q(t)$ stands for the accumulated charge at time t and D represents the ionic diffusion coefficient. ΔQ is the total intercalated charge for corresponding voltage step and l is the thickness of the oxide layer. The Cottrell region will be observed in the time dependence plot of $Q(t)t^{-1/2}$ for each voltage step and the diffusion coefficient can be estimated.

Figure 4.8a presents the time dependence of $Q(t)t^{-1/2}$ for the four voltage steps. Each step exhibits the same curve features in the time dependence plot. The curve start from a low value of $Q(t)t^{-1/2}$, which is due to the kinetic limitation from the diffusion process.^{103, 104} The magnitude of $Q(t)t^{-1/2}$ starts to increase with time (region I) and reaches the lowest point of the curve (region II), which is the time independent region – Cottrell region. After the Cottrell region, the $Q(t)t^{-1/2}$ starts to decrease due to the finite space effect. With the increase in the time, the intercalation sites are mostly occupied, which results in the small Q value while $Q(t)t^{-1/2}$ decreases towards zero. Theoretically, a plateau corresponding to the Cottrell region is expected in region II.

However, similar to other reported PITT experiments,^{105, 106} there is only a narrow Cottrell region being detected in the actual experiment, which is the minimum point in region II.

Figure 4.8b summarizes the diffusion coefficient of Li^+ in the non-porous and macroporous WO_3 film. Both samples exhibit similar decreasing trend in the diffusion coefficient at the more negative voltage. The decreasing trend can be explained through the percolation model proposed by Vertes et al.¹⁰⁷. There are two types of diffusion channel in the transition metal oxide electrode: one with faster diffusivity while the other is slower. At a more negative voltage, the Li^+ intercalation level increases and the volume fraction of the fast diffusivity channel decreases. The diffusion coefficient of the slow diffusivity channel dominates the overall diffusion coefficient and hence smaller diffusion coefficient is detected at more negative voltages where the Li^+ intercalation level is higher. However, the further details regarding the physical nature of the two channels require additional investigation. As shown in Figure 4.8b, the non-porous and macroporous WO_3 films both exhibit similar value of diffusion coefficient. The coefficient varies between $1 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ to $5 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ for the four voltage steps and possesses an average value around $6.9 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$. These coefficients are comparable to other reported values in the WO_3 (Table 4.2). Since both samples exhibit similar value of diffusion coefficient, we can conclude that the diffusion coefficient of Li^+ within the WO_3 is not affected by the macroporous structure. The enhancement in the electrochemical and EC performances should be dominated by the shortening in the ionic diffusion distance.

Figure 4.8 (a) The time dependence of $Q(t)t^{-1/2}$ for the four voltage steps ranging from -0.15 V to -0.35 V (vs. Ag/AgCl), (b) the diffusion coefficient in macroporous and non-porous WO_3 film.

Table 4.2 Li^+ diffusion coefficient in WO_3

D_{Li} ($\text{cm}^2 \text{s}^{-1}$)	Reference
1.85×10^{-9}	¹⁰⁸
6.10×10^{-10}	This work
4.50×10^{-10}	⁹³
4.00×10^{-11}	¹⁰⁵
3.00×10^{-11}	¹⁰⁹

4.7 Effects of oxide morphology on ion intercalation process

The ion intercalation process in transition metal oxide has been reported by Crandell et al.¹¹⁰, which includes the ion injection through the oxide-electrolyte interfac

e and follows by the solid state ionic diffusion across the oxide lattice. Both processes can be affected by tailoring the oxide into macroporous structure. Firstly, the oxide-electrolyte interfacial area has been increased in the macroporous structure. This provides additional reaction sites for ion injection into WO_3 lattice per unit time. This has resulted in the higher amount of total stored charge in macroporous structure (Section 4.3). Secondly, the ionic diffusion distance is shortened in the macroporous structure. The solid state diffusion process can be completed in shorter time and hence the switching time can be improved (Section 4.4). Coupling the advantages from these two aspects, the macroporous WO_3 film has become a promising electrode for EC application.

Figure 4.9 Schematic views of the (a) non-porous and (b) macroporous WO_3 during the Li^+ intercalation.

Figure 4.9 presents the schematic view of the WO_3 films during Li^+ intercalation to further illustrate the ion intercalation in non-porous macroporous oxide layer. In section 4.6, the diffusion coefficients of Li^+ in non-porous and macroporous WO_3 film are found to be similar in magnitude. In another words, in unit time, the solid state ionic diffusion distance of Li^+ in both samples are the same. This will lead to the formation of similar volume of Li_xWO_3 from the oxide-electrolyte interface, which contain W^{5+} and is responsible for the blue colour during the coloration state. In Figure 4.9a, the Li_xWO_3 is formed at the region just underneath the oxide-electrolyte interface and the inner part of WO_3 film is inactive as the Li^+ has not diffused to this region. In contrast, the electrolyte penetration has delivered the Li^+ to the inner part of the oxide in the macroporous film (Figure 4.9b). Once the electrons are injected into the WO_3 , the total volume of Li_xWO_3 in the macroporous film will be larger than the non-porous film. Comparing the two cases, it is clearly that the macroporous

structure is more effective in forming the Li_xWO_3 , whereas the Li^+ can be intercalated through the whole WO_3 layer within short duration. This has resulted in the overall enhancement in the reaction kinetic, creating more instant optical response upon the electrical signal and the increase in the total stored charge. The macroporous WO_3 film is hence a promising EC electrode with better capacitance, less lagging in the optical responses, higher CE and faster switching.

4.8 Summary

In this chapter, the effects of oxide morphology on electrochromic (EC) performances and electrochemical reaction have been investigated. Through tailoring the WO_3 film into macroporous structure, the capacitance, switching times, and coloration efficiency (CE) are greatly improved as compared to the non-porous WO_3 film. The detailed mechanisms of these enhancements have been discussed from two aspects: ionic diffusion in oxide lattice and ion intercalation process. In summary, the electrochemical redox reaction is the key factor that governs the electrochemical performances and it is significantly affected by the ionic diffusion process in the oxide lattice. The macroporous WO_3 film exhibits such promising performance is due to the following unique characteristics in the macroporous structure:

- 1) Porous structure with connecting pathways: electrolyte can penetrate into the inner parts of the oxide layer. The ionic diffusion distance and diffusion time are hence shortened and lead to better reaction kinetic.
- 2) Large oxide-electrolyte interface: a complete redox reaction requires the injection of cation across the oxide-electrolyte interface. In macroporous structure, the large interfacial area has provided more reaction sites and facilitates the ion injection / extraction.
- 3) Short ionic diffusion distance: The slow ionic diffusion process in the oxide lattice has limited the performances of transition metal oxide. The shortening in the diffusion distance can significantly reduce the diffusion time and improves the reaction kinetic.

Chapter 5 Effects of metal doping on electrochemical reactions and charge storage in transition metal oxide

5.1 Introduction

In Chapter 4, the effects of oxide morphology and dimension on charge carriers' transportation during the redox reaction have been studied. Through forming nanoscale oxide (around 100 nm), the interfacial area and ion diffusion distance can be controlled to enhance the electrochemical reactions. Apart from the oxide morphology and dimension, the electrochemical reactions in transition metal oxide can also be enhanced through doping conductive metal into the oxide lattice. The metal doping could improve electronic conductivity of the semi-conductive transition metal oxides.⁸³⁻⁸⁵ This will lead to better charge transfer rate and enhance the overall reaction kinetic. Moreover, the doped metal ions can also take part in the redox reaction during the voltage biasing and contribute additional charges. This will result in better charge storage and specific capacitance (SC). However, there are also some possible disadvantages associated with metal doping. Since part of the redox reaction is diffusion controlled process, the presence of the doped metal ions in the oxide lattice could hinder the cation diffusion and slow down the diffusion process. In addition, the metal doping could also alter the oxide lattice structure. For example of layered structure V_2O_5 , the interlayer spacing, which serves as the cation diffusion path, is found to decrease after the metal doping.^{83, 111} This variation in the oxide lattice structure can affect the cation diffusion process and results in inferior electrochemical redox reaction. Hence, the effects of metal doping on electrochemical reactions and charge storage are investigated in this chapter to verify the above

viewpoints. Metal doping could be a promising method in improving the performances if the above drawbacks can be controlled.

In order to facilitate the metal doping and electrochemical reaction, a host material with large and easy access lattice spacing is preferred. Vanadium oxide (V_2O_5), which possesses a promising specific capacitance up to 350 F g^{-1} ,⁵³ is selected as the materials of choice in our studies. V_2O_5 possesses a unique oxide lattice structure which is composed of VO_5 square pyramid layers and the layers are connected by weak Van der Waal force. The layered structure has provided the flexibility in accommodating metal ions^{83, 111, 112} or even polymer molecules⁸². Moreover, the interlayer spacing serves as the cation diffusion pathway as well as the ion intercalation sites. This unique layered structure could facilitate the cation diffusion and provide sufficient intercalation sites for the purpose of charge storage. In literatures, V_2O_5 has been doped with various metal dopants, including Li, Na, K, Ag, Cu, Cr, Mn and Mo (summarized in Table 5.1). These reports have proved that V_2O_5 exhibits enhanced electronic conductivity, cycling stability and capacitance after the metal doping. In summary, a promising dopant should fulfil two criteria: high electronic conductivity and large ionic radius. High electronic conductivity is required to further improve the electronic conductivity of the semi-conductive V_2O_5 while the large ionic radius helps to create large interlayer spacing to facilitate the ion diffusion. Hence, the electronic conductivity and ionic radius of these dopants are compared in Table 5.1.

Table 5.1 Various dopants in V₂O₅ and respective electronic conductivity and ionic radius. The values in bold are the three highest ionic radius and electronic conductivity.

Dopant	Electronic conductivity (S m⁻¹)	Ionic radius (pm)
Li ^{113, 114}	1.08 x10 ⁷	90
Na ^{2, 113}	2.10 x10⁷	116
K ¹¹³	1.39 x10 ⁷	152
Ag ^{83, 84, 115, 116}	6.30 x10⁷	129
Cu ^{83, 112, 117-119}	5.96 x10⁷	87
Cr ^{35, 111}	7.90 x10 ⁶	75.5
Mn ^{120, 121}	5.00 x10 ⁵	78
Mo ¹²²⁻¹²⁴	1.73 x10 ⁷	75

Based on Table 5.1, Ag has been selected as the dopant for our studies because of its highest electronic conductivity and large ionic radius.

In this chapter, the effects of Ag doping on electrochemical reaction and charge storage mechanism are investigated. Detailed studies in the redox reaction of Ag and V are carried out through cyclic voltammetry (CV) and X-ray photoelectron spectrometer (XPS) analysis. Scan rate dependence analysis is also carried out to identify the effects of Ag doping on the rate capability of the V₂O₅. Lastly, we demonstrate a specially designed electrode which combines the advantages from the two oxide modification strategies: oxide structural dimensionality (Chapter 4) and metal doping (this chapter). The electrochemical performances of this electrode confirmed that the combined strategies achieve promising performances.

5.2 Structural characterization of V_2O_5 based nanobelts

Figure 5.1 FESEM and TEM (insets) images of (a) un-doped and (b) Ag doped V_2O_5 nanobelts, (c) EDX spectrum of un-doped V_2O_5 and Ag doped V_2O_5 nanobelts.

Un-doped and Ag doped V_2O_5 nanobelts are synthesized through hydrothermal process. Figure 5.1 displays the FESEM and TEM images of the un-doped and Ag doped V_2O_5 nanobelts. The nanobelt widths of both samples are controlled to be around 16 nm (± 2 nm) to achieve similar surface area for comparison in the electrochemical performances before and after Ag doping. As compared to other reported hydrothermally synthesized V_2O_5 based nanobelts / nanoribbons (width around 200 to 800 nm),^{116, 125-127} the Ag doped nanobelts in this work are much smaller with uniform size distribution. This serves to provide larger surface to volume ratio and shorter ionic diffusion distance, which are the desired criteria as an electrode material. The nanobelts are drop-casted onto ITO glass and forming nanobelt network with pores for electrolyte penetration. Energy dispersive X-ray (EDX) studies have been carried out to identify the existing elements in the nanobelts. The EDX spectrum (Figure 5.1c) of Ag doped V_2O_5 nanobelts has confirmed the presence of Ag with a doping level of 0.79 per V_2O_5 .

Figure 5.2 Schematic view of ion diffusion distance in nanobelts structure with (a) thickness and (b) width perpendicular to the electric field.

Although the nanobelts possess the length in several micrometers, the ion diffusion distance in this study is bounded by the nanobelt width, which is less than 20 nm. Figure 5.2 illustrates the ion diffusion distance in the nanobelts. As the nanobelts are drop-casted onto the ITO glass and not a free standing array, the nanobelts are positioned on the ITO surface with either the thickness (Figure 5.2a) or width (Figure 5.2b) (quasi-) perpendicular to the electric field. The cations are moving under the driving force from the electric field, which is parallel to the electric field direction. Hence, the maximum ion diffusion distance that needs to be concerned is the width of the nanobelts.

Figure 5.3 displays the X-ray diffraction (XRD) patterns of the un-doped and Ag doped V_2O_5 nanobelts. Both nanobelts are crystalline and the peaks can be attributed to the (00 l) series of peaks in the layered hydrate of V_2O_5 (PDF# 40-1297). The V_2O_5 hydrate is composed of layers of VO_5 square pyramids with the water molecule contained between the layers. (001) peak in the XRD pattern of layered hydrate structure represents the interlayer distance and it varies with different water level^{2, 82} or intercalated substance.^{2, 116} The (001) peak of un-doped V_2O_5 nanobelts is located at 9.04° , which corresponds to an interlayer distance of $9.8 \text{ \AA}$. On the other hand, the

(001) peak of Ag doped V_2O_5 nanobelts is located at 11.56° , which corresponds to an interlayer distance of $7.8 \text{ \AA}$. The smaller interlayer distance in the Ag doped V_2O_5 nanobelts could be due to two reasons. Firstly, the Ag doped V_2O_5 nanobelts could have lower water content as compared to the un-doped V_2O_5 nanobelts, which have resulted in a less expanded interlayer spacing. Secondly, the metal doping tends to form stronger connection between the layers and reduces the interlayer spacing.⁸³

Figure 5.3 X-ray diffraction (XRD) patterns of un-doped and Ag doped V_2O_5 nanobelts.

Figure 5.4 Thermal-gravimetric analyses (TGA) of un-doped and Ag doped V₂O₅ nanobelts in N₂ ambient. The heating rate is 10 °C min⁻¹.

Figure 5.4 shows the thermal-gravimetric analysis (TGA) of un-doped and Ag doped V₂O₅ nanobelts. Weight loss is observed in the un-doped V₂O₅ nanobelts starting from room temperature to 350 °C. The total weight loss in un-doped V₂O₅ nanobelts is 14 %. In contrast, the Ag doped V₂O₅ nanobelts only exhibit a well defined weight loss of 8 % between 250 °C to 350 °C. As shown in the XRD results, both nanobelts are V₂O₅ based hydrate. The weight loss in the two samples can hence be attributed to the removal of water molecule in the hydrate structure¹¹⁶ or the physically absorbed water.⁸² The un-doped V₂O₅ nanobelts contain higher level of bounded water, which agrees well with the observation of larger interlayer distance in the XRD results. The different behaviours in weight loss in the two nanobelt samples can be attributed the Ag doping. The metal doping in the V₂O₅ has been found to improve the structural stability of the layered structure.^{2, 111, 112} The metal ions tend to connect two layers and stabilize the layered structure. Hence, the water removal in Ag doped V₂O₅ nanobelts only occur at higher temperature.

5.3 Electrochemical redox reactions and charge storage in metal doped V₂O₅ nanobelts

Cyclic voltammetry (CV) was carried out to investigate the electrochemical reactions of the un-doped and Ag doped V₂O₅ nanobelts within potential window of ± 0.5 V (vs. Ag/AgCl) in 1.0 M LiClO₄/PC electrolyte. There are three types of electrochemical reactions upon the voltage biasing, which contribute to the charge storage. The first reaction is electrical double layer (EDL), which is a non-Faradic reaction involving the charge separation in the electrolyte. The cations and anions in the electrolyte are separated and attached to the oxide electrode surface with opposite polarity and formed the EDL at the oxide-electrolyte interface. The second reaction is also occurring at the oxide-electrolyte interface. In contrast to the EDL, this reaction is a redox reaction and is a Faradic reaction, where charge transfer occurs between the transition metal and surface atom. The third reaction is a Faradic redox reaction that involves the injection / extraction of ions at the oxide-electrolyte interface and solid state diffusion within the oxide lattice.^{1,4} The second reaction and third reaction are both redox reactions, which can be expressed as (in Li⁺ electrolyte):

In equation 5.1, x represents the Ag doping level of 0 (un-doped nanobelts) and 0.79. On the other hand, y stands for the total intercalation level of Li⁺ contributed from the second and third reaction. y is also equivalent to the number of electrons involved in the redox reaction per Ag_xV₂O₅ since each electron corresponds to one Li⁺ for charge neutrality.

Figure 5.5 Cyclic voltammograms of un-doped and Ag doped V_2O_5 nanobelts at 5 mV s^{-1} scan rate. Electrolyte: $1.0 \text{ M LiClO}_4/\text{PC}$.

Figure 5.5 displays the cyclic voltammograms of un-doped and Ag doped V_2O_5 nanobelts at 5 mV s^{-1} scan rate. The un-doped V_2O_5 nanobelts exhibit rectangle shape CV curve without any well defined redox peak during the voltage cycling. Similar CV curve feature have also been observed in the $V_2O_5 \cdot nH_2O$ sample reported by Lee *et al.*⁵³ In contrast, the Ag doped V_2O_5 nanobelts exhibit well defined redox peaks with one reduction peak at -0.27 V and two oxidation peaks at -0.23 V and $+0.01 \text{ V}$. The current density in the Ag doped V_2O_5 nanobelts is larger than the un-doped nanobelts. This has resulted in higher total charge stored in the nanobelts, which is represented by the area under the CV curve and can be represented by the Li^+ intercalation level in the nanobelts. The Li^+ intercalation level in the un-doped nanobelts is 0.25 per V_2O_5 . In contrast, the Li^+ intercalation level in Ag doped V_2O_5 nanobelts is 0.64 per $\text{Ag}_{0.79}V_2O_5$, which is 2.6 times larger than the un-doped V_2O_5 nanobelts.

Figure 5.6 Scan rate dependence specific capacitance of un-doped and Ag doped V_2O_5 nanobelts for scan rate ranging from 5 mV s^{-1} to 100 mV s^{-1} . Electrolyte: $1.0 \text{ M LiClO}_4/\text{PC}$.

The specific capacitance (SC, F g^{-1}) of the nanobelt samples can be calculated based on the CV curve through the equation:

$$SC = \frac{Q}{m\Delta V} \quad (5.2)$$

where Q stands for the total stored charge (C), m represents the mass of the electrode material and ΔV is the potential window. Figure 5.6 displays the SC of un-doped and Ag doped V_2O_5 nanobelts for scan rate ranging from 5 mV s^{-1} to 100 mV s^{-1} . At 5 mV s^{-1} , the un-doped V_2O_5 nanobelts exhibit a SC of 134 F g^{-1} . This SC is comparable to the reported V_2O_5 based 1D nanostructures.^{128, 129} On the other hand, the Ag doped nanobelts show an improved SC up to 198 F g^{-1} , which is around 1.5 times of the un-doped nanobelts. Since there is more than one type of electrochemical reactions in the transition metal oxide, the enhancement in SC could be the combine effect from several aspects. Firstly, with the Ag doping in the nanobelts, the Ag ions may take

part in the redox reaction and contribute additional charges, which would result in higher stored charge and SC. The second possible reason is relevant to the redox reaction which occurs at the oxide-electrolyte interface. The capacitance per unit area of this reaction could be enhanced after the Ag doping (such as having better electronic conductivity and hence the higher charge transfer rate).^{83, 116} Lastly, the diffusion coefficient can be improved after the metal doping in the transition metal oxide.⁸⁴ In this case, faster cation diffusion can be achieved in the oxide lattice, which results in higher charge contribution per unit time (i.e. under constant scan rate).

The possibility of additional charge contribution from Ag ions can be verified through XPS analysis on the nanobelt samples at different oxidation and reduction voltage, which will be discussed in Section 5.4. The charge contributions can be verified through the scan rate dependence analysis based on their different reaction mechanism and time dependence. The analysis serves to quantify the capacitance contribution from each type of redox reaction, which will be presented in Section 5.5. In addition, the basic factors which govern the two types of redox reaction (i.e. the electronic conductivity and ion diffusion process) are also studied to provide insights on the reaction mechanism after the Ag doping (Section 5.6).

The scan rate dependence SC is presented in Figure 5.6. The SC of both samples decreases with the increase in scan rate, which is due to the kinetic limitation in the electrochemical reactions at short duration of time (i.e. fast scan rate). There is a slight degradation in SC of Ag doped V_2O_5 nanobelts at 5 mV s^{-1} . This degradation implies that Ag doped nanobelts have degraded in the prolonged charging and discharging process at 5 mV s^{-1} . However, the SC degradation at slow scan rate has not been observed in other V_2O_5 based electrodes.^{2, 130} This drop in SC could be associated to the presence of irreversible redox reaction. Comparing the intercalation and de-

intercalation charge at 5 mV s^{-1} , the un-doped nanobelts exhibit 6 C g^{-1} of irreversible charges, which corresponds to 5% of its total stored charge. In contrast, the Ag doped nanobelts are six times higher in the irreversible charge. The Ag doped nanobelt exhibits 35 C g^{-1} of irreversible charges, which corresponds to 13 % of the total stored charges. This higher irreversible charges could be due to the smaller interlayer distance after the Ag doping (as shown in the XRD study, Figure 5.3), where the ion de-intercalation is less facile as compared to the un-doped V_2O_5 nanobelts. The rate capabilities of the un-doped and Ag doped nanobelts can be determined from Figure 5.6. At all scan rates, Ag doped V_2O_5 nanobelts are at least 64 F g^{-1} higher than the un-doped nanobelts. Since the Ag doped nanobelts degraded at 5 mV s^{-1} , it is improper to evaluate the SC retention with respect to the SC at 5 mV s^{-1} . Hence, the SC retention is calculated based on the SC at 10 mV s^{-1} as:

$$SC \text{ retention} = \frac{SC_{100\text{mVs}^{-1}}}{SC_{10\text{mVs}^{-1}}} \times 100\% \quad (5.3)$$

The un-doped nanobelts exhibit a SC retention of 56 % at 100 mV s^{-1} . In contrast, the Ag doped nanobelts possess better charge storage capability at high scan rate, which is reflected as the better SC retention of 72 % at the same scan rate. In short, after the Ag doping, the rate capability of the V_2O_5 nanobelts has been significantly improved, where the SC of the Ag doped nanobelts is generally higher under the same scan rate and the SC retention is better at high scan rate.

5.4 Electrochemical redox reaction in metal doped V_2O_5 nanobelts

Figure 5.7 CV curve of Ag doped V_2O_5 nanobelts at 5 mV s^{-1} scan rate. The samples are charged or discharged to different oxidation and reduction voltages as shown in the figure before subjected to XPS analysis. Electrolyte: $1M\ LiClO_4/PC$.

Figure 5.7 presents the CV curve of Ag doped V_2O_5 nanobelts at 5 mV s^{-1} scan rate. The CV curve exhibits a reduction peak and two oxidation peaks, which implies that there may be more than one type of redox reaction taking place in the Ag doped V_2O_5 nanobelts. Moreover, as discussed in Section 5.3, there are two types of metal ion in the Ag doped V_2O_5 nanobelts (i.e. Ag and V), the enhancement in the SC after the Ag doping could be due to the additional charge contribution from Ag ions. XPS analysis was carried out to understand the details in the redox reaction and the charge contribution in the Ag doped V_2O_5 nanobelts. Based on the CV curve in Figure 5.7, four samples were subjected to different reduction or oxidation voltages for XPS analysis to investigate the bonding oxidation states of Ag and V. The first nanobelt samples is discharged to -0.1 V, which is at the voltage before the reduction peak

(Red -0.1 V). On the other hand, the second samples is discharged to -0.4 V, which is at the voltage after the reduction peak (Red -0.4V V). These two samples provides information on the reduction process in Ag doped V_2O_5 nanobelts. The third and fourth sample are firstly discharged to -0.5 V and then charged to different oxidation voltage. The third sample is charged to -0.1 V, which is at the voltage after the first oxidation peak (Ox -0.1 V). The fourth sample is charged to +0.2 V, which is at the voltage after the second oxidation peak (Ox +0.2 V). The third and fourth samples are used to study the oxidation in the Ag doped V_2O_5 nanobelts.

5.4.1 Reduction

Figure 5.8 displays the high resolution XPS spectrum of sample (Red -0.1 V) and (Red -0.4 V). O 1s spectrum (Figure 5.8a) of both samples can be deconvoluted into two peaks located at 530.0 eV and 531.7 eV. The peak at 530.0 eV is corresponding to the metal-oxide binding within the oxide lattice.¹³¹ On the other hand, the peak located around 531.7 eV arises from the H_2O molecule², which could be contributed from the hydrates (as shown in XRD and TGA analysis) or surface absorbed water. Figure 5.8b shows the V 2p spectra of (Red -0.1 V) and (Red -0.4 V), which correspond to the sample with the discharging voltage before and after the reduction peak, respectively. The BE of V 2p_{3/2} of the sample before the reduction peak is found to be 516.8 eV, which can be attributed to the V^{5+} .^{115, 132} An additional peak at 519.6 eV is also observed in the V 2p region. This peak can be attributed to the V 2p satellite peak, which has been reported having BE ranging from 514 eV to 530 eV in literatures.¹³³⁻¹³⁷ In contrast, after the reduction peak, the V 2p_{3/2} peak can be deconvoluted into two peaks at 516.8 eV and 514.6 eV, which can be attributed to V^{5+}

^{115, 132} and V^{4+} , ¹³⁸ respectively. The presence of V^{4+} after the reduction peak confirms that the V^{5+} state is partially reduced to V^{4+} . Investigation on the Ag peak was also carried out as the Ag possesses several oxidation states (Ag^0 , Ag^{1+} and Ag^{2+}) and could take part in the redox reaction. Ag 3d spectra before (Red -0.1 V) and after (Red -0.4 V) the reduction peak are shown in Figure 5.8b. Different from the V 2p spectra, the Ag 3d_{5/2} peak of the two samples remain at the same BE around 367.9 eV before and after the reduction peak, which corresponds to +1 oxidation state of Ag.^{85, 115} The result clearly indicates that the Ag ions are not involved in the reduction process and do not contribute additional charges for charge storage. Hence, the charge contribution during the reduction should be solely attributed to the reduction of V^{5+} to V^{4+} .

Figure 5.8 High resolution XPS spectra for (a) O 1s and V 2p and (b) Ag 3d region of samples at (Red -0.1 V) and (Red -0.4 V).

5.4.2 Oxidation

Figure 5.9 shows the high resolution XPS spectrum of sample (Ox -0.1 V) and (Ox +0.2 V), which correspond to the nanobelts charged at the voltage after the first and second oxidation peak, respectively. Similar to the observation in Section 5.4.1, the O 1s spectra of both samples can be deconvoluted into two peaks, which arise from the metal-oxide bonding (530.0 eV) and H₂O (531.7 eV). High resolution V 2p spectra of the two nanobelt samples are displayed in Figure 5.9b. For the sample after the first oxidation peak (Ox -0.1 V), the V 2p_{3/2} peak can be deconvoluted into two peaks at 516.8 eV and 514.6 eV, which correspond to V⁵⁺ and V⁴⁺, respectively. The presence of V⁴⁺ after the oxidation peak implies that only partial V⁴⁺ is oxidized back into V⁵⁺ during the first oxidation peak. On the other hand, the V 2p_{3/2} peak of the fourth samples can be deconvoluted into 516.8 eV (V⁵⁺) and 514.6 eV (V⁴⁺), which suggests that there are some residual V⁴⁺ presences after the second oxidation peak. These residual V⁴⁺ is resulted from the quasi-reversible redox reaction in V₂O₅, where some V⁵⁺ are permanently reduced to V⁴⁺. This observation can be verified by comparing the Li⁺ intercalation and de-intercalation charge of the CV curve, which correspond to the charges involved in the reduction of V⁵⁺ and oxidation of V⁴⁺, respectively. As shown in the CV curve of 150 °C synthesized Ag doped nanobelts in Figure 5.7, the Li⁺ intercalation charge of nanobelts (from +0.5 V to -0.5 V) is 0.27 C mg⁻¹ while the Li⁺ de-intercalation charge (from -0.5 V to +0.5V) is 0.23 C mg⁻¹. The smaller Li⁺ de-intercalation charge suggests that the redox reaction is quasi-reversible and some V⁵⁺ has been irreversibly reduced into V⁴⁺.

Figure 5.9 High resolution XPS spectrum for (a) O 1s and V 2p and (b) Ag 3d region of sample (Ox -0.1 V) and (Ox +0.2 V).

XPS investigation on the Ag was also carried out to identify whether the Ag are oxidized from Ag¹⁺ to Ag²⁺ upon the oxidation voltage. The Ag 3d spectra of the two nanobelt samples are displayed in Figure 5.9b. The Ag 3d_{5/2} peaks of both samples remain as a single peak around 367.9 eV, which corresponds to the +1 oxidation state. This indicates that the Ag ions do not take part in the oxidation, the oxidation charge is solely contributed by the two steps oxidation of V⁴⁺. Hence, we can conclude that the oxidation of V⁴⁺ in Ag doped V₂O₅ nanobelts is a two-step process.

In summary, the redox peak in the CV curve of Ag doped V_2O_5 nanobelts arises from the redox couple of V^{5+}/V^{4+} and Ag does not involve in the redox reaction. Therefore, based on these results, we can conclude that the enhancement in SC after the Ag doping (as compared to the un-doped V_2O_5 nanobelts) is not due to the additional charge contribution from Ag ions.

5.5 Surface dependent and diffusion controlled redox reaction in metal doped V₂O₅ nanobelts

In Section 5.3, we have discussed three electrochemical reactions, which contribute to the total charge stored in the transition metal oxide, namely the non-Faradic reaction EDL, Faradic redox reaction of charge transfer at oxide-electrolyte interface and diffusion controlled Faradic redox reaction in oxide lattice. These electrochemical reactions possess different reaction mechanism and time dependence, which help to identify and quantify the charge and hence the capacitance contribution from different reactions. The EDL and surface charge transfer are surface dependence reaction, which take place at the oxide-electrolyte interface. These two reactions possess capacitive response and are inversely proportional to time. In cyclic voltammetry studies, this time dependence translates to the relationship in scan rate ($V s^{-1}$). The current, i , for scan rate, v , can be expressed as: ¹¹

$$i = ACv \quad (5.4)$$

where A is the electrochemical active surface area (cm^2) and C is the capacitance per unit area ($C cm^{-2}$).

The redox reaction occurs in the oxide lattice and is depending on the diffusion of cation. This diffusion controlled reaction is inversely proportional to the square root of time and directly proportional to the square root of scan rate in cyclic voltammetry as: ¹³⁹

$$i = nFAC^*\sqrt{D}\sqrt{\pi}\sqrt{\alpha nF/RT}\chi(bt)\sqrt{v} \quad (5.5)$$

where n is the no of electron involved per redox reaction, F is the Faraday constant, A stands for the electrochemical active surface area, C^* is the ion concentration in the

electrolyte, D represent the chemical diffusion coefficient of the ion, α is the transfer coefficient, R is the gas constant, T is the temperature and $\chi(bt)$ function represents the current function for the redox reaction.

At any voltage in the CV curve, the current at that particular voltage is contributed from these two types of reaction, which can be expressed in term of scan rate (v) as: ^{1, 2}

$$i = k_1 v + k_2 \sqrt{v} \quad (5.6)$$

where k_1 and k_2 are the proportionality constants of surface dependence reaction and diffusion controlled reaction. The current contributed from these two reactions can hence be determined by knowing the k_1 and k_2 , the corresponding charge contributions and capacitances can be calculated. Through carrying out CV at different scan rates, the k_1 and k_2 at different voltage can be estimated from the slope and intersection point in $(i/\sqrt{v})$ vs. $(\sqrt{v})$ plot, according to the following equation (based on equation 5.6):

$$\frac{i}{\sqrt{v}} = k_1 \sqrt{v} + k_2 \quad (5.7)$$

The voltammetric responses of un-doped and Ag doped V_2O_5 nanobelts at 5 mV s^{-1} scan rate are shown in Figure 5.10. The k_1 and k_2 are estimated based on the CV curve with scan rates ranging from 5 mV s^{-1} to 20 mV s^{-1} . In the un-doped V_2O_5 nanobelts (Figure 5.10a), the currents at the two vertexes of the CV curve are mainly contributed from the diffusion controlled reaction while the middle region is dominated by the surface dependent reaction. This observation is similar to the result reported by Brezesinski *et al.* in CeO_2 .¹⁴⁰ The voltammetric responses of Ag doped V_2O_5 nanobelts are shown in Figure 5.10b. The regions around redox peaks are

dominated by the diffusion controlled reaction while the surface dependent reaction contributes the current of the rest of the region. Similar distribution has been reported for the transition metal oxide with well defined redox peaks, such as V_2O_5 ², TiO_2 ¹,¹⁴¹ and MoO_3 .¹⁴² The total stored charge and the corresponding SC can hence be determined from the area under the CV curve.

Figure 5.10 Voltammetric responses of the (a) un-doped and (b) Ag doped V_2O_5 nanobelts at 5 mV s^{-1} . The shaded region is contributed by the surface dependent reaction while the white region under the CV curve corresponds to the diffusion controlled reaction.

Figure 5.11 SC contribution from surface dependent reaction and diffusion controlled reaction at 5 mV s^{-1} .

Figure 5.11 illustrates the relative contribution in SC from the surface dependent reaction and diffusion controlled reaction at 5 mV s^{-1} . The SC contributed from the surface dependent reaction and diffusion controlled reaction are named as “surface dependent capacitance” and “intercalation capacitance”, respectively. In un-doped V_2O_5 nanobelts, the surface dependent and intercalation capacitance are similar in magnitude, which contribute 53 % and 47 % of total SC, respectively. After the Ag doping, the surface dependent capacitance is significantly improved to 129 F g^{-1} , which is around 1.6 times of the surface dependent capacitance in un-doped nanobelts. The total SC is more dominated by the surface dependent reaction after the Ag doping, which has contributed 64 % of the total SC. The surface dependent capacitance is depending on the oxide-electrolyte interfacial area and the capacitance per unit area. The increase in surface dependent capacitance, after the Ag doping, can be attributed to three possible reasons: 1) the additional charge contribution from the Ag ions, 2) the difference in morphology or dimension which could increase the oxide-electrolyte

interfacial area and 3) the increase in the capacitance per unit area. Since we have proven that the morphology and dimension of the un-doped and Ag doped nanobelts are similar (section 5.2) and the Ag ions are not involved in the redox reaction and contribute additional charges (Section 5.4), the first and second reason can be excluded. This capacitance enhancement should hence be attributed to the higher capacitance per unit area, which is affected by the charge transfer rate after the Ag doping. As shown in equation 5.1, the charge transfer process of the redox reaction requires the presence of two charge carriers: electrons and cations. During reduction, the electrons are injected from the ITO glass into the oxide layer while the cations are injected from the electrolyte. Similarly, during oxidation, the electrons are extracted through ITO glass and the cations are expelled back to electrolyte. Hence, the higher electronic conductivity or ion diffusion coefficient could enhance the charge transfer rate by having faster movement for charge carriers in the oxide lattice. This means that the charge transfer in the Ag doped nanobelts per unit time will be increased and resulted in higher capacitance (per unit area) within the same potential window and time duration (i.e. same scan rate). In order to study the transportation of the two charge carriers, four points probe and potentiostatic intermittent titration technique (PITT) have been carried out and the details are presented in Section 5.6.

We have found earlier that the rate capability of the Ag doped V_2O_5 nanobelt has been significantly improved after the Ag doping (section 5.3). After the Ag doping, the surface dependent capacitance is significantly improved to 129 F g^{-1} , which contributes 64 % of the total SC. As we have discussed, the surface dependent reaction is a capacitive reaction and is a faster reaction as compared to the slow diffusion controlled reaction. With the increased contribution in the SC, surface reaction dominates the overall electrochemical reaction. Hence, with the increase in

scan rate (i.e. decrease in the reaction time), the Ag doped nanobelts can exhibit faster response as compared to the un-doped nanobelts, which reflects in the higher SC and better SC retention at high scan rates.

5.6 Electron and ion transportation in the un-doped and metal doped V₂O₅ nanobelts

After Ag doping, the surface dependence capacitance in the nanobelts is increased and contributed up to 64 % of the total SC. The reason of this enhancement is attributed to the better charge transfer rate after the Ag doping, which could due to the improved electronic conductivity and/or ion diffusion coefficient.

5.6.1 Electron transportation

In literatures, metal doping in V₂O₅ (such as Ag⁺, Cu²⁺) thin film^{83, 85} and xerogel⁸⁴ has been reported to show one or two orders increase in the electronic conductivity. The enhancements in the total stored charge and capacitance in these metal doped V₂O₅ have been attributed to the better charge transfer rate after the doping. Similar situation could also occur in our Ag doped nanobelts. In order to verify this, four point probe study has been carried out to compare the electronic conductivities in the un-doped and Ag doped V₂O₅ nanobelts. The un-doped V₂O₅ nanobelts possess electronic conductivity of $2.6 \times 10^{-2} \text{ S cm}^{-1}$. This conductivity is one to two orders higher in magnitude as compared to the V₂O₅ thin films^{83, 84} and comparable to the V₂O₅ xerogel.⁸⁵ In contrast, the Ag doped V₂O₅ nanobelts exhibit an enhanced electronic conductivity of $2.0 \times 10^{-1} \text{ S cm}^{-1}$. This conductivity is one order higher than the un-doped nanobelts and comparable to the other reported Ag doped V₂O₅ based materials.⁸³⁻⁸⁵

Figure 5.12 I-V testing of single nanobelt (deposited across Au electrodes): a) Un-doped nanobelt and b) Ag doped nanobelt. [Insets: the FESEM images of the single nanobelt on Au electrode.]

Current-Voltage (I-V) study has also been carried out on single nanobelt to further study the electron transportation in the un-doped and Ag doped nanobelt. The un-doped and Ag doped nanobelt are deposited across Au electrode with channel length around 4 μm (Insets in Figure 5.12). Both samples are in Schottky contact with the Au electrode. The forward biased current of Ag doped nanobelt is found to be around one order higher as compared to the un-doped nanobelt.

Based on the I-V curves in Figure 5.12, the Schottky barrier (ϕ_B) of the nanobelts can be extracted by plotting current density vs. the applied forward bias voltage (Figure 5.13). For a metal-semiconductor contact, the current density (J) - voltage (V) characteristic is given by ¹⁴³ :

$$J = J_s(e^{qV/kT} - 1) \quad (5.8)$$

and

$$J_s = A^*T^2e^{-q\phi_B/kT} \quad (5.9)$$

where J_s is the saturation current density, ϕ_B is the Schottky barrier, T is the absolute temperature and q , k , A^* are the Boltzmann constant, elementary charge and Richardson constant, respectively. By extrapolating the forward J-V curve to $V=0$ (Figure 5.13), the J_s can be found and hence the barrier height (ϕ_B) can be calculated using equation 5.9.¹⁴³ The un-doped nanobelt possesses a Schottky barrier height of 0.23 V and this barrier height has been reduced to 0.16 V after the Ag doping. This observation is in good agreement with other reported metal doped semiconductors where the barrier height can be effectively lowered through metal doping.¹⁴⁴⁻¹⁴⁶ The results have clearly shown that Ag doping can reduce the barrier height and result in higher current density at forward bias. The presence of Ag in the nanobelt has facilitated the electron transportation and hence the charge transfer rate in the nanobelt.^{83, 116} This is in agreement with the higher surface dependent capacitance and better rate capability as observed after the Ag doping in V_2O_5 nanobelts (as shown in Section 5.5).

Figure 5.13 I-V plot of single nanobelt: a) Un-doped nanobelt and b) Ag doped nanobelt at forward bias.

5.6.2 Ion transportation

The ion transportation in oxide lattice is a diffusion process and significantly affected by the ion diffusion coefficient. The ion diffusion coefficient is affected by the size of the cation and the oxide lattice, which defines the presence of diffusion pathway and the size of the available vacancies among the atoms. In this study, we are focusing on the diffusion of Li^+ in un-doped and Ag doped V_2O_5 , which possess a layered structure with interlayer spacing acting as the diffusion pathway. As shown in the XRD results (Section 5.2), both un-doped and Ag doped V_2O_5 nanobelts are layered structure but with different interlayer distances of 9.8 Å and 7.8 Å, respectively. The diffusion coefficient could be affected in two ways after the Ag doping: 1) the presence of Ag hinders the diffusion of Li^+ and 2) the smaller interlayer distance results in slower diffusion. In order to verify whether the Ag doping has altered the ion diffusion in the oxide lattice, potentiostatic intermittent titration technique (PITT) was applied to obtain the diffusion coefficient of the un-doped and Ag doped V_2O_5 nanobelts. The diffusion coefficients are calculated from the Cottrell region of all voltage steps based on the equation 4.4 and summarized in Figure 5.14.

Figure 5.14 The diffusion coefficients in un-doped and Ag doped V_2O_5 nanobelts for five voltage steps.

The diffusion coefficients of the un-doped nanobelts vary between $1 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ and $4 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ with an average value of $2.6 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$. After the Ag doping, the diffusion coefficients remain similar with an average value of $2.9 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$. The results imply that the Ag doping does not significantly impact on the ion diffusion in the nanobelts. This implies that the improved charge transfer rate after the Ag doping should be attributed to the increase in the electronic conductivity while the ion diffusion coefficients remain similar.

5.7 Coupling the effects from oxide dimension and metal doping

In Chapter 4, the advantages from smaller oxide dimension and larger surface to volume ratio in the electrochemical reaction have been clearly illustrated through comparing the bulk and mesoporous transition metal oxide. In addition, the advantages of metal doping have also been demonstrated in the previous sections in this chapter. It is possible to combine the advantages arise from the two modifications to further enhance the performance. We have specifically prepared V_2O_5 nanobelts which possess similar Ag doping level but with smaller nanobelt width as compared to the Ag doped nanobelts presented in previous sections. Structural characterization, cyclic voltammetry and scan rate dependence analysis are carried out to illustrate the effects of the resulted nanobelts.

5.7.1 Structural characterization

The Ag doped V_2O_5 nanobelts presented in previous sections are displayed in Figure 5.15a. These nanobelts were synthesized at 150 °C and exhibit nanobelt widths around 16 nm. Through lowering the hydrothermal temperature, nanobelts with smaller width can be prepared. Figure 5.15b shows the nanobelts which were synthesized at lower hydrothermal temperature of 120 °C with the width around 10 nm. EDX spectra of the 150 °C and 120 °C synthesized nanobelts (Figure 5.15c) confirm the successful Ag doping in the nanobelts and the Ag doping level are 0.79 and 0.78 per V_2O_5 , respectively. The 120 °C synthesized nanobelts possess similar Ag doping level but a smaller nanobelt width, which can provide a larger oxide-electrolyte interfacial area and shorter ion diffusion distance. In addition, the nanobelts are drop casted onto the

ITO glass, which are in a network configuration with sufficient connected pathways for electrolyte penetration.

Figure 5.15 FESEM and TEM (insets) images of (a) 150 °C and (b) 120 °C synthesized Ag doped V_2O_5 nanobelts, (c) EDX spectrum of 150 °C and 120 °C synthesized Ag doped V_2O_5 nanobelts.

Figure 5.16a displays the XRD patterns of the 150 °C and 120 °C synthesized nanobelts. The 120 °C synthesized nanobelts exhibit diffraction peak at the same 2 θ angles as the 150 °C synthesized nanobelts. The diffraction peaks in both samples can be labelled as the (00*l*) series peaks in the V_2O_5 based hydrate (PDF# 40-1297) with an interlayer distance of 7.8 Å. Despite of the (00*l*) series peak, the 120 °C synthesized nanobelts exhibit an additional low intensity peak at 9.02 °. This peak can be attributed to the (001) plane of the un-doped V_2O_5 nanobelts which corresponds to an interlayer spacing of 9.8 Å (Section 5.2). The low relative intensity of this peak implies the presence of small amount of un-doped V_2O_5 nanobelts during the hydrothermal synthesis. This could due to the incomplete Ag doping in the nanobelts at lower temperature since the hydrothermal temperature was lowered from 150 °C to 120 °C to produce nanobelts with smaller dimension.

Figure 5.16 (a) X-ray diffraction (XRD) patterns and (b) thermal-gravitational analysis (TGA) of 150 °C and 120 °C synthesized Ag doped V₂O₅ nanobelts.

Figure 5.16b shows the TGA curve of the 150 °C and 120 °C synthesized nanobelts. Both samples exhibit a well defined weight loss at 250 °C to 350 °C region with similar weight loss varying between 8 % and 10 %. The result suggests that the Ag doped nanobelts still possess similar thermal-gravitational behaviour and water content, despite their different synthesis temperature and nanobelt width.

Table 5.2 summarized the electronic conductivities and diffusion coefficients of Li⁺. The electronic conductivities are obtained through four points probe study while the diffusion coefficient is the average value from five voltage steps in the PITT study.

Table 5.2 Electronic conductivities and diffusion coefficients of Li^+ of 150 °C and 120 °C synthesized Ag doped V_2O_5 nanobelts.

	Electronic conductivity	Diffusion coefficient
Ag doped V_2O_5 (150°C)	$1.9 \times 10^{-1} \text{ S cm}^{-1}$	$2.9 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$
Ag doped V_2O_5 (120°C)	$2.2 \times 10^{-1} \text{ S cm}^{-1}$	$3.5 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$

Both electronic conductivity and diffusion coefficient of the 150 °C and 120 °C synthesized Ag doped nanobelts are similar in magnitude. The results suggest that the difference in nanobelt dimension does not significantly affect the electronic conductivity and diffusion coefficient, which govern the “speed” of the electron and ion transportation in the oxide lattice, respectively.

5.7.2 Electrochemical redox reactions and charge storage

Figure 5.17a displays the cyclic voltammograms of 150 °C and 120 °C synthesized Ag doped V_2O_5 nanobelts at 5 mV s^{-1} . The 120 °C synthesized nanobelts exhibit a reduction peak at -0.32 V and two oxidation peaks at -0.22 V and +0.04 V, which are similar to CV curve of the 150 °C synthesized nanobelts, except with a larger current density. The result implies that similar redox reactions occur in the 120 °C synthesized nanobelts with higher charge contribution from the reactions, which have resulted in higher current density and larger area under the CV curve.

Figure 5.17 (a) Cyclic voltammograms and (b) scan rate dependence specific capacitance (SC) of 150 °C and 120 °C synthesized Ag doped V_2O_5 nanobelts.

The 150 °C synthesized nanobelts have 0.64 Li^+ intercalated per $Ag_{0.79}V_2O_5$. In contrast, the 120 °C synthesized nanobelts possess 0.84 Li^+ intercalation per $Ag_{0.78}V_2O_5$, which is 1.3 times higher as compared to the 150 °C synthesized nanobelts. Figure 5.17b shows the scan rate dependence SC of the nanobelts. Similar to previous observation, the 120 °C synthesized nanobelts also exhibit the highest SC at 10 $mV s^{-1}$ with a degraded SC at 5 $mV s^{-1}$. With the reduction in nanobelt width, the SC of 120 °C synthesized nanobelts has significantly increased up to SC of 308 $F g^{-1}$, which is around 1.6 times higher than the 150 °C synthesized nanobelts (at 5 $mV s^{-1}$). Moreover, the rate capability of the 120 °C synthesized nanobelts is also significantly enhanced. The SC of the 120 °C synthesized nanobelts is at least 100 $F g^{-1}$ higher than the 150 °C synthesized nanobelts across the all scan rates. At 100 $mV s^{-1}$, the 120 °C synthesized nanobelts can exhibit a high SC of 262 $F g^{-1}$. This SC is higher than the 3D porous $V_2O_5 \cdot nH_2O$ film (175 $F g^{-1}$)¹³⁰, V_2O_5 - SnO_2 -CNT composite (121 $F g^{-1}$)¹⁴⁷ and β - $Na_{0.33}V_2O_5$ nanobelts (220 $F g^{-1}$)² at 100 $mV s^{-1}$ and other reported values at slow scan rate.^{52, 128, 129} As compared to the 150 °C synthesized nanobelts, the SC of

120 °C synthesized nanobelts is around 100 F g⁻¹ higher and show a better SC retention up to 78 % at 100 mV s⁻¹.

The increase in the SC and the promising rate capability in Ag doped V₂O₅ nanobelts could be due to several reasons associated with the reduce in nanobelt width. Firstly, additional charge contribution could arise from Ag ions if there is a significant difference in Ag doping level between the nanobelt samples. Secondly, the electrochemical active surface area between the oxide and electrolyte (per unit mass) is expected to increase with the reduction in nanobelt width. This serves to provide more reaction sites for the surface dependent reaction and hence increase the surface dependent capacitance. Moreover, the relative contribution from fast reaction could also be increased and leads to enhancement in the overall reaction kinetic and hence the better rate capability. The third possible reason is regarding the diffusion distance in the diffusion controlled redox reaction. As discussed in Section 5.2, the limiting ion diffusion distance is equal to the nanobelt width. With the reducing in the width, the ion diffusion distance is shortened and the diffusion time is reduced. This could also enhance the rate capability since shorter diffusion time is required for the intercalation process.

The first reason can be excluded in current study as the EDX results have confirmed the similar Ag doping level in both samples. For the second and third reason, scan rate dependence analysis can be employed to verify and quantify the corresponding capacitance from each reaction. The magnitude of the corresponding SC and the ratio between them will provide a comprehensive explanation to the enhancements in SC and rate capability after reducing the nanobelt width.

5.7.3 Scan rate dependence analysis

Figure 5.18 Voltammetric responses of (a) 150 °C and (b) 120 °C synthesized Ag doped V₂O₅ nanobelts at 5 mV s⁻¹, (c) relative ratio between surface dependent capacitance and intercalation capacitance.

The scan rate dependence analysis was carried out from 5 to 20 mV s⁻¹ and the voltammetric responses of the 150 °C and 120 °C synthesized Ag doped V₂O₅ nanobelts are displayed in Figure 5.18a and 5.18b, respectively. Both CV curves exhibit similar current distribution. The currents from diffusion controlled reaction (i.e. Li⁺ intercalation within the oxide lattice) mainly occur at the voltages around redox peaks while the surface dependent reaction contributes the current in the rest of

the voltage region. Based on the currents' magnitude, the capacitance contribution from the two reactions can be calculated. The relative contribution in SC from the surface dependent reaction (i.e. surface dependent capacitance) and diffusion controlled reaction (i.e. intercalation capacitance) are summarized in Figure 5.18c. After reducing the nanobelt width, the surface dependent capacitance in 120 °C synthesized nanobelts has significantly increased up to 255 F g⁻¹. This capacitance is around 2 times higher than the 129 F g⁻¹ in 150 °C synthesized nanobelts. The enhancement clearly indicates that the nanobelt with smaller dimension and larger oxide-electrolyte interfacial area can effectively increase the surface dependent capacitance. On the other hand, the intercalation capacitance remains similar in value regardless of the variation in the nanobelt width. This observation implies that the performance enhancement through reducing in the ion diffusion distance has certain limit. Reducing the nanobelt width from 16 nm to 10 nm cannot further enhance the ion diffusion process or increase the Li⁺ intercalation level.

As discussed in Section 5.5, the relative contribution of capacitance from surface dependent reaction and diffusion controlled reaction is affecting the rate capability. In 150 °C synthesized nanobelts, the promising rate capability is due to the surface dependent capacitance which has contributed up to 64 % of the total SC. The slow diffusion controlled reaction has been “replaced” by the fast surface reaction, which provides better rate capability.^{1, 2} The rate capability in the 120 °C synthesized nanobelts is further enhanced with the surface dependent reaction which contributes up to 78 % of the total SC. This further enhancement is attributed to the reduction in nanobelt width, which has increased the reaction sites and promoted the surface dependent reaction. The overall electrochemical reaction is hence dominated by the fast surface reaction and leads to better rate capability.

5.8 Summary

The effects associate with metal doping on electrochemical reaction and charge storage have been demonstrated in this chapter. The electrochemical reaction in V_2O_5 is altered where well defined redox peaks arise after the Ag doping. On the other hand, the enhancements in the electronic conductivity and charge transfer rate (due to the Ag doping) have promoted the surface dependent reaction. This has resulted in larger current density and hence higher Li^+ intercalation level and specific capacitance (SC) as compared to the un-doped V_2O_5 nanobelts. Moreover, the overall electrochemical reaction in the V_2O_5 nanobelts is found to be dominated by the fast surface dependent reaction, which has significantly enhanced the rate capability of the nanobelts.

Ag doped V_2O_5 nanobelts with smaller width have also been prepared to show the advantages from reduced oxide dimension and metal doping. After reducing the width of the Ag doped nanobelt, both SC and rate capability of the nanobelts are significantly enhanced. The surface dependent reaction is found to be further promoted as more oxide-electrolyte interfaces are created with the reduction of nanobelt width. This has resulted in higher charge contribution from the surface dependent reaction, which increased the SC and Li^+ intercalation level. The rate capability is also enhanced as the relative capacitance contribution from surface dependent reaction is further increased with the smaller nanobelt width. The overall electrochemical reaction is dominated by the fast surface reaction and exhibits promising reaction kinetic and rate capability.

In summary, the SC and rate capability can be enhanced through:

- 1) Promoting the surface dependent reaction to achieve higher amount of total stored charge. This will increase the SC and Li^+ intercalation level in the transition metal oxide.
- 2) Replacing the slow diffusion controlled reaction with the fast surface dependent reaction. Promising rate capability with high SC and good SC retention at high scan rate can be achieved by having the surface dependent reaction dominating the overall electrochemical reaction.

Chapter 6 Effects of oxide lattice structure on electrochemical reactions and charge storage in transition metal oxide.

6.1 Introduction

In Chapter 4 and Chapter 5, the effects of oxide morphology and dimension and metal doping have been discussed with detailed analysis during the electrochemical reactions. The advantages associated with the two oxide modifications have significantly enhanced the surface dependent reaction and diffusion controlled reaction in transition metal oxide, which is reflected in the promising specific capacitance (SC) and rate capability. In previous chapters, the performance comparisons are carried out on the samples with similar oxide lattice structure. This means that the intercalation sites and diffusion pathway in the samples are similar.

The oxide lattice structure plays an important role which governs the electrochemical performances. As discussed in previous chapters, the charge contribution in the transition metal oxide is mainly arises from the redox reaction (including the charge transfer at the oxide-electrolyte interface and diffusion controlled reaction), which involved the intercalation and de-intercalation process of the cation. Hence, the oxide lattice structure, which determines the diffusion pathway and intercalation sites, is an important criterion in designing a high SC and good rate capability electrode. An oxide lattice with fast diffusion pathway will be preferred to facilitate the diffusion process and promote the diffusion controlled reaction through improving the diffusion coefficient or diffusion time. However, transition metal oxide could possess several kinds of oxide lattice structure and exhibit different types of diffusion pathway. For

example, MnO_2 can exist as layered and framework structure, the diffusion pathways could be planar ($1 \times \infty$) or tunnel (1×1 , 1×2 and spinel structure) structure depending on the oxide lattice structure of the MnO_2 .^{148, 149}

In addition, the intercalation sites within oxide lattice are also important during the ion intercalation process. A promising oxide lattice with good rate capability should possess accessible intercalation sites with suitable volume for ion accommodation. Moreover, the differences in intercalation site could affect the intercalation voltage (such as the redox peak in CV) and hence the potential window for actual application. Lastly, the amount of intercalation site is also crucial as it determines the ion intercalation, which directly affects the total stored charge and SC of the material.

In this chapter, the effects of oxide lattice structure on the electrochemical reaction and charge storage performance are investigated from two aspects: ion intercalation sites and ion diffusion pathway. Metal doped V_2O_5 nanobelts with similar dimension but different oxide lattice structure are employed as the study material. Na doped V_2O_5 nanobelt is selected for this study as it can exist in layered structure² and three-dimensional framework structure (β -phase) (upon Na doping).^{2, 150}

The oxide lattice structure of the layered V_2O_5 nanobelts is displayed in Figure 6.1. The layered structure is composed of square pyramid (VO_5) layers with V locating at within the pyramid and surrounded by five oxygen atoms.¹¹⁴ The square pyramids are weakly tilted due to the O-O repulsion force at the apex of the square pyramids. The pyramids are connected in corners and edges sharing and aligned in zigzag pattern while the adjacent square pyramid layers are connected by Van der Waals force (Figure 6.1).¹⁵¹ The weak interlayer connection force has provided flexibility for ion^{83, 111, 112} or polymer molecule^{82, 116} intercalation since the layers can be easily

expanded and provide sufficient volume for the intercalation. Besides accommodating the intercalated substance, the interlayer spacing also serves as diffusion pathway during ion diffusion. These pathways are located along a and b direction, which has formed a 2D diffusion pathway network between the layers.

Figure 6.1 Oxide lattice structure of layered V_2O_5 based material (a) along y axis and (b) with intercalated substance (hollow circles) between VO_5 layers.¹¹⁴

On the other hand, the β -phase is a three dimensional framework structure composed of square pyramids (VO_5) and connected in corner and edge sharing (Figure 6.2).¹⁵⁰ A tunnel, which parallel to $[010]$, is formed with the surrounding of VO_5 square pyramid while the Na ions are located at the middle of the tunnel. This β -phase framework structure can be formed through the phase transformation of layered structure. Similar to the layered structure which possesses interlayer spacing as the fast diffusion pathway, the framework structure possesses a tunnel as the diffusion pathway with the metal ion (i.e. Na) located at the middle of tunnel.

Figure 6.2 Oxide lattice structure of framework V_2O_5 based material (along direction $[010]$).¹⁵⁰

In this chapter, cyclic voltammetry and scan rate dependence analysis are carried out to investigate the effects of oxide lattice structure on the surface dependent reaction and diffusion controlled reaction. Correlation to the SC and rate capability of the nanobelt electrode is also established based on these electrochemical studies.

6.2 Structural characterization on Na doped V₂O₅ nanobelts

Figure 6.3 X-ray diffraction patterns of as-synthesized and annealed Na doped V₂O₅.

The as-synthesized product is air-annealed at 300 °C to form β -phase framework structure. Figure 6.3 presents the X-ray diffraction patterns of the as-synthesized and annealed Na doped V₂O₅. The as-synthesized product exhibits typical characteristics of V₂O₅ based hydrate, where the peaks can be attributed to the (00 l) series and the (001) peak possesses a high relative intensity due to the lamella structure in the V₂O₅ hydrate (PDF# 40-1297). The (001) peak in the XRD pattern of layered structure V₂O₅ identifies the interlayer distance between the adjacent layers.¹⁵² The (001) peak of the as-synthesized nanobelts is located at 10.56 °, which corresponds to a interlayer distance of 8.36 Å and is close to the interlayer distance of 8.75 Å in V₂O₅ · 0.5 H₂O (PDF# 40-1297). After annealing, the Na doped V₂O₅ exhibits a completely different XRD pattern. The presence of new peaks implies that a new phase has been formed through the annealing process. The peaks in the XRD pattern of the annealed nanobelts can be assigned to the peaks in β -Na_{0.33}V₂O₅ (PDF# 24-1155). This β phase

Na doped V_2O_5 possess a framework structure with a tunnel for ion intercalation and diffusion.

Figure 6.4 FESEM images of the Na doped V_2O_5 nanobelts (a) before and (b) after annealing.

Figure 6.4 displays the FESEM images of the as-synthesized and annealed Na doped V_2O_5 . The as-synthesized product (Figure 6.4a) is in nanobelt form with 100 to 150 nm in width, 50 nm in thickness and more than 10 μm in length. After the annealing, the Na doped V_2O_5 still remains in nanobelt form and there is no significant variation in the nanobelts' dimension. Both nanobelt samples are drop-casted onto the substrate to form a nanobelt network structure with interconnected nanobelts and pores for electrolyte penetration. As shown in Section 5.2, the maximum ion diffusion distance of nanobelt network structure is the width of the nanobelt. Since there is no significant difference in the nanobelt dimension before and after the annealing, the ion diffusion distance of layered (as-synthesized nanobelts) and framework (annealed, β -phase nanobelts) structure are both around 100 to 150 nm.

6.3 Phase transformation of layered structure nanobelts upon annealing

Thermal-gravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS) study are carried out on the as-synthesized and annealed nanobelts. TGA will provide information regarding the water content and water removal at elevated temperature. In addition, the XPS study can confirm the Na doping and study the water removal and oxidation states of the elements before and after the annealing.

Figure 6.5 Thermal-gravimetric analysis (TGA) of the Na doped V_2O_5 nanobelts from room temperature to 500 °C in N_2 ambient at heating rate of 10 °C per minute.

Thermal-gravimetric analysis (TGA) of the Na doped V_2O_5 nanobelts is shown in Figure 6.5. Two significant weight losses are detected during the heating from room temperature to 500 °C, which is similar to the multiple weight losses in $V_2O_5 \cdot nH_2O$ xerogels.¹⁵³ The first weight loss between 100 °C to 150 °C can be attributed to the removal of physically bounded water at the nanobelts surface.⁸² On the other hand, the second weight loss between 200 °C to 300 °C can be attributed to the removal of

chemically bounded water within the nanobelt hydrate.^{82, 116} The second weight loss (i.e. water removal) is around 5 wt%, which corresponds to 0.49 H₂O per Na_{0.33}V₂O₅. This observation signifies that the phase transition during annealing is associated with the water removal from the as-synthesized nanobelt hydrate. The slight increase in weight at 450 °C to 500 °C is also observed. This increase could be due to the formation of V₃O₈ based material at elevated temperature.¹⁵⁴⁻¹⁵⁶ The V₃O₈ based material contain higher amount of oxygen (O:V = 2.67) than V₂O₅ based material (O:V = 2.50). This additional oxygen could have induced the slight increase in weight at elevated temperature.

Figure 6.6a displays the XPS wide range scan of the as-synthesized and annealed Na doped V₂O₅ nanobelts. The spectra confirm the successful Na doping in the as-synthesized nanobelts, which is completed during the hydrothermal process. Figure 6.6b shows the high resolution XPS spectra of V 2p and O 1s region. Single V 2p_{3/2} peak is detected in the as-synthesized nanobelts, which is located around 517.0 eV and corresponds to V⁵⁺.¹³⁸ After annealing, a shoulder occurs at the V 2p_{3/2} peak and the peak can be deconvoluted into two peaks at 517.3 eV and 516.0 eV, which correspond to V⁵⁺ and V⁴⁺, respectively.¹³⁸ The presence of V⁴⁺ implies that V⁵⁺ is partially reduced to V⁴⁺ during annealing. The O 1s spectra of the as-synthesized nanobelts can be deconvoluted into two peaks at 529.9 eV and 532.0 eV. The peak at 529.9 eV is corresponding to the metal-oxide bonding in V₂O₅^{131, 138} while the peak around 532.0 eV can be attributed to the bonding in H₂O molecule,² which could arise from the chemically bounded water in the hydrate or physically bounded water at nanobelt surface (as shown in the TGA results). The relative intensity of the peak arises from water molecule is found to decrease after the annealing. This observation

has further confirmed the water removal during the annealing and supported the TGA results.

Figure 6.6 X-ray photoelectron spectroscopy (XPS) spectra of as-synthesized and annealed Na doped V_2O_5 nanobelts: (a) wide range scanning and (b) high resolution spectra at V 2p and O 1s region.

In summary, Na doping in V_2O_5 nanobelts takes place during the hydrothermal process and the as-synthesized nanobelts are hydrate with 0.49 H_2O . During the annealing, phase transformation occurs associated with the removal of water in the hydrate. The Na doped V_2O_5 nanobelts have successfully transformed from layered structure (as-synthesized nanobelts) into β phase framework structure (annealed nanobelts), which possess a tunnel with Na locating at the middle of the tunnel, through annealing the as-synthesized layered structure Na doped V_2O_5 . The phase transition in the Na doped V_2O_5 nanobelts can be summarized as the following equation:

6.4 Formation of β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$ nanobelts

The observations in Section 6.2 and 6.3 have clearly indicated that the formation of β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$ nanobelts is due the water removal and phase transformation upon 300 °C air annealing. There are some new questions arise with this conclusion: What are the criteria that required to form framework structure? Are the Na doping and annealing essential in forming the framework structure and how does a layered structure transform into a framework structure? A reference to the phase diagram of $\text{M}_x\text{V}_2\text{O}_5$ bronze (M represents the doping ions) helps to understand the existence of difference phases in V_2O_5 system and the criteria of forming the framework structure.

Figure 6.7 Phase diagram of $\text{M}_x\text{V}_2\text{O}_5$ bronze (In this phase diagram, the doping ion is Li).^{114, 151}

Figure 6.7 shows the phase diagram of $\text{M}_x\text{V}_2\text{O}_5$ bronze (M represents the doping ions), where the β -phase framework structure can be formed with two criteria: correct

doping level and elevated temperature. The requirement in specific doping level is due to the stabilization in the framework structure. The framework structure can still exist if the doping level is only slightly deviated from this value, which reflects as the β -phase region in the phase diagram. The stoichiometric doping level of the framework structure (Figure 6.6) is 0.33 for Na doping and the XRD study has confirmed the annealed Na doped nanobelts are β -Na_{0.33}V₂O₅ (Section 6.2). The phase diagram also suggests that the formation of β -phase occurs at elevated temperature. This is because the transformation from layered structure into framework structure requires energy in the re-arrangement of square pyramid slabs.

Figure 6.8 shows the transformation from layered structure to framework structure with the presence of doping ion (dashed circle). The VO₅ square pyramids layers are sliced into slabs 1 and 2 by crystallographic shear (Figure 6.8a). These slabs ended with oxygen vacancy (indicated as square in Figure 6.8b). The oxygen in the slabs 1 and 2 are rearranged (following the curved arrows) and the whole slab slips along the straight arrows and stacks together. The alternate repetition of the stacked slabs 1 and 2 constructs the framework structure with a tunnel along the [010] direction.

Figure 6.8 Transformation process from layered structure to framework structure in V_2O_5 based system (a) slicing the VO_5 layers into slabs 1 and 2 by crystallographic shear and (b) re-arrangement of the slabs and forming framework structure.¹⁵¹

Similar to the layered structure, the β -phase framework structure also possesses fast diffusion pathway for the ion diffusion during electrochemical reaction, which is the tunnel in the framework structure. In addition, the spacing in the tunnel serves as the intercalation site. Different from the layered structure, the framework structure possesses up to three types of geometrically accessible intercalation sites along the tunnel, including an intercalation site at the middle of the tunnel (M_1), an eight coordinated intercalation site (M_2) and a tetrahedral intercalation site (M_3).^{150, 157} These three sites are labelled in framework structure in Figure 6.6 and the schematic view of each site is displayed in Figure 6.9. Since there are more than one type of intercalation sites in the framework structure, the full intercalation process in the framework structure could be complicated and composed of multiple steps, which could be detected as the multi-plateau region during the galvanostatic discharging or more than one set of redox peak in the CV curve.¹⁵⁸

Figure 6.9 The intercalation sites within the tunnel of the β -phase framework structure (a) intercalation site at the middle of the tunnel (M_1 site), (b) eight coordinated site (M_2 site) and (c) tetrahedral site (M_3 site). The solid circle represents the intercalated cation while the hollow circle represents the oxygen atoms.¹⁵⁰

Both layered and framework structures are promising oxide lattice structures for electrochemical application. Both structures possess fast diffusion pathway for ion diffusion and intercalation sites to accommodate ions during the electrochemical reaction. However, the difference in of intercalation site in layered and framework structure has caused some variations in electrochemical reaction, which are reflected in the CV curve. These differences directly affects the total stored charge (i.e. area under the CV curve) and hence the SC. Moreover, the rate capability is also altered

since the electrochemical reactions in the layered and framework structure vary and possess different reaction kinetic. In order to investigate the effects of oxide lattice structure on electrochemical reaction and charge storage performances, cyclic voltammetry (CV) and scan rate dependence analysis are carried out and presented in Section 6.5 and 6.6, respectively.

6.5 Electrochemical reaction and charge storage in layered and framework structure

Figure 6.10 Cyclic voltammograms of layered and framework structure Na doped V_2O_5 nanobelts. Electrolyte: 1 M $LiClO_4/PC$.

Cyclic voltammetry was carried out to study the electrochemical reactions in the layered and framework structure Na doped V_2O_5 nanobelts for potential window of ± 0.5 V. The redox reaction, which accompanied with the Li^+ intercalation / de-intercalation in the Na doped V_2O_5 nanobelts, can be expressed as:

where x represents the number of electrons involved per reaction and the Li intercalation level. As shown in Figure 6.10, the layered structure nanobelts exhibit one set of redox peak, where the reduction and oxidation peaks are located at -0.36 V and -0.21 V, respectively. In contrast, the framework structure nanobelts possess two sets of redox peak. The reduction peaks are located at $+0.08$ V and -0.23 V while the oxidation peaks are located at $+0.33$ V and -0.21 V. Both nanobelt samples exhibit

similar current densities, which vary between $\pm 3 \text{ A g}^{-1}$ in the CV curve. However, the two sets of redox peak in the framework structure nanobelts have resulted in larger area under the CV curve, which represents the higher amount of total charge stored in the nanobelts. The area under the CV curve can be used to calculate Li^+ intercalation level in the nanobelts. The layered structure nanobelts possess an intercalation level of 0.38 while the framework structure nanobelt exhibits an intercalation level of 0.66, which is 1.7 times higher as compared to the layered structure nanobelts.

As shown in Section 6.4, the intercalation site in the layered structure nanobelts is located at the interlayer spacing between two adjacent square pyramid layers. The redox peak in the CV curve can hence be attributed to the intercalation and de-intercalation of Li^+ at this intercalation site. On the other hand, the framework structure nanobelts possess three types of intercalation site along the tunnel; including an intercalation site at the middle of the tunnel (M_1), an eight coordinated intercalation site (M_2) and a tetrahedral intercalation site (M_3). The M_1 site is initially half occupied by the Na^+ ions (i.e. the Na doping).¹⁵⁰ The full Li^+ intercalation process in the rest of the intercalation sites is composed of three intercalation steps. The first intercalation step occurs at intercalation level $0 < x < 0.33$, where the M_3 sites is half occupied by the Li^+ . The second intercalation step take place at intercalation level $0.34 < x < 0.70$, where the M_2 sites is half occupied by the Li^+ . The last intercalation step occurs at intercalation level $0.75 < x < 1.65$, where all the remaining intercalation sites of M_1 , M_2 and M_3 are fully occupied. The intercalation level between $0.33 < x < 0.34$ and $0.70 < x < 0.75$ are the transition region among the intercalation steps with Li^+ intercalation continuously occurring.^{157, 158}

The overall Li^+ intercalation level on the framework structure nanobelts is 0.66 in $\pm 0.5 \text{ V}$ potential window at 5 mV s^{-1} . This means only the first and second

intercalation steps take place at the current potential window and scan rate, which correspond to the half occupancy of M3 and M2 site. The third intercalation step ($0.75 < x < 1.65$) is not detected in current scan rate, likely due to the slow diffusion of Li^+ at $x > 0.70$, where the diffusion coefficient is found to be two to four orders smaller at $x > 0.70$.¹⁵⁸

Figure 6.11 Scan rate dependence specific capacitances (SC) of layered and framework structure Na doped V_2O_5 nanobelts.

Figure 6.11 displays the SC of the layered and framework structure Na doped V_2O_5 nanobelts from 5 mV s^{-1} to 100 mV s^{-1} . At 5 mV s^{-1} , the layered structure nanobelts exhibit a SC of 191 F g^{-1} . In contrast, the framework structure nanobelts possess SC of 320 F g^{-1} , which is 1.7 times higher as compared to the layered structure nanobelts. This SC is also comparable or higher than the reported crystalline V_2O_5 based nanostructures.^{128, 129, 159} The layered structure nanobelt exhibits a promising rate capability where SC of 143 F g^{-1} can be achieved at 100 mV s^{-1} , which corresponds to

SC retention of 75 %. On the other hand, the framework structure nanobelts exhibit better rate capability. The SC of the framework structure nanobelts is at least 50 F g^{-1} higher than the layered structure nanobelts across the scan rates. In addition, the framework structure nanobelts can achieve 191 F g^{-1} at 100 mV s^{-1} , which corresponds to SC retention of 60 %.

As shown in Chapter 5, the SC and rate capability is significantly affected by surface dependent reaction and diffusion controlled reaction. The capacitance contribution from each reaction determines the overall SC while the ratio between these two capacitances (i.e. surface dependent capacitance and intercalation capacitance) affects the rate capability. Based on the same principle, the enhancement in SC and rate capability, which associated with the phase transition from layered structure to framework structure, can be attributed to the following reasons:

- 1) Diffusion pathway: the presence of fast diffusion pathway in oxide lattice can facilitate the ion diffusion. This could increase the intercalation capacitance and improve the rate capability through shortening the required diffusion time.
- 2) Intercalation sites: The presence of easy accessible intercalation sites can increase both surface dependent capacitance and intercalation capacitance as the redox reaction, which requires the intercalation of Li^+ ions, involving both the surface dependent reaction and diffusion controlled reaction (Equation 6.2).

This can be verified through quantifying the surface dependent capacitance and intercalation capacitance in layered and framework structure nanobelts. This can be achieved through scan rate dependence analysis, which is presented in next section (Section 6.6).

6.6 Surface dependent reaction and diffusion controlled reaction in layered and framework structure Na doped V_2O_5 nanobelts

Figure 6.12 Voltammetric responses of (a) layered and (b) framework structure Na doped V_2O_5 nanobelts at 5 mV s^{-1} scan rate. The solid line represents the total current. The shaded region is contributed by the surface dependent reaction while the white region is contributed by the diffusion controlled reaction. (c) Relative SC contribution from surface dependent reaction and diffusion controlled reaction.

Figure 6.12a and 6.12b display the voltammetric responses of the layered (as-synthesized) and framework (annealed) structure Na doped V_2O_5 nanobelts at 5 mV s^{-1} scan rate. The current contribution from surface dependent and diffusion controlled reaction are determined based on the different scan rate dependence of the respective

reaction.^{1, 11, 139} Although the layered and framework structure nanobelts possess different electrochemical reaction and CV curve features, both nanobelt samples exhibit similar distribution in the currents contributed from surface dependent reaction and diffusion controlled reaction. The currents around the redox peaks are mainly contributed from the diffusion controlled reaction (the white region) while the rest of the voltage range are dominated by the surface dependent reaction (shaded region). Similar current distributions have also been observed in other transition metal oxides, including V_2O_5 ,² TiO_2 ,^{1, 141} and MoO_3 .¹⁴²

Figure 6.12c shows the relative SC contribution from surface dependent reaction and diffusion controlled reaction, which are calculated based on the voltammetric responses in Figure 6.12a and 6.12b. In the layered structure nanobelts the surface dependent capacitance (contributed by the surface dependent reaction) and intercalation capacitance (contributed by the diffusion controlled reaction) are around 142 F g^{-1} and 58 F g^{-1} , which correspond to 71 % and 29 % of the total SC, respectively. Similar to the observations in layered structure Ag doped V_2O_5 nanobelts (Chapter 5), the overall reaction in the layered structure Na doped V_2O_5 nanobelts is dominated by the surface dependent reaction, which has resulted in the promising SC and rate capability. In contrast, the framework structure nanobelts exhibit 193 F g^{-1} surface dependent capacitance and 127 F g^{-1} intercalation capacitance, which contribute 60 % and 40 % of the total SC, respectively. As compared to the layered structure nanobelts, the magnitude of SC in the framework structure nanobelts has been further improved in both surface dependent capacitance and intercalation capacitance, especially the intercalation capacitance is almost doubled. The result implies that, at similar oxide morphology and dimension, the

framework structure is more effective in promoting the surface dependent and diffusion controlled reaction.

Although the surface dependent reaction dominates the overall reaction in both layered and framework nanobelts, the contribution from the surface dependent in total SC has decreased from 71 % to 60 % after the phase transition from layered structure to framework structure. In addition, the SC retention of the framework structure nanobelts is found to decrease at high scan rate. These two observations can be correlated. Since the surface dependent reaction is less dominating in the framework structure nanobelts, the kinetics limitation of the diffusion controlled reaction will be more significant at high scan rate as the diffusion controlled reaction requires longer reaction time and cannot contribute large amount of charges within a short duration (i.e. at high scan rate). Even though the framework structure possesses smaller SC retention, the SC across the scan rates are still generally 50 F g^{-1} higher than the SC of layered structure nanobelts. This is due to the framework structure has promoted both surface dependent and diffusion controlled reaction, which has increased the amount of total stored charge as compared to the layered structure nanobelts under the same scan rate.

In summary, the framework structure nanobelts exhibit better SC than the layered structure nanobelts. Despite of the slightly inferior SC retention, the rate capability of the framework structure nanobelts is still promising as it can store more charges under same scan rates. These promising performances should be attributed to the advantages associated with the framework structure where there is a tunnel diffusion pathway and up to three types of easy accessible intercalation sites are present along the tunnel. These unique features have significantly promoted both surface dependent and

diffusion controlled reaction and resulted in better reaction kinetic and charge storage performances.

6.7 Summary

In this chapter, Na doped V_2O_5 nanobelts with layered and framework structure are used to demonstrate the effects of oxide lattice structure on electrochemical reaction and charge storage behaviours. With similar morphology and dimension, the framework structure Na doped V_2O_5 nanobelts ($\beta\text{-Na}_{0.33}V_2O_5$) are found to exhibit electrochemical reactions different from the layered structure nanobelts, due to their differences in ion intercalation sites. Moreover, the framework structure nanobelts are more effective in charge storage as it possesses three geometrical accessible ion intercalation sites along the tunnel in the framework lattice structure. This has resulted in superior ion intercalation level and specific capacitance (SC) in framework structure nanobelts. In terms of rate capability, the layered structure nanobelts possess better SC retention while the framework structure nanobelts exhibit higher amount of total charge stored under the same scan rate. The better SC retention in the layered structure nanobelts is due to the domination of surface dependent reaction, which is a faster reaction as compared to the diffusion controlled reaction. On the other hand, the unique framework structure, which possesses three types of ion intercalation site and a tunnel along [010] direction as the fast diffusion pathway, has promoted both surface dependent and diffusion controlled reaction. This has increased the charge contribution from both reactions and hence the SC under the same scan rate.

Chapter 7 Conclusion and future works

7.1 Summary

The studies in this thesis have focused on the electrochemical reactions in transition metal oxide and the demonstration of enhanced performances for electrochemical redox device application. The transition metal oxides have unique reversible redox reaction and allow optical modulation at different oxidation states. The transition metal ions provide significant amount of charge during the redox reaction, which is attractive for electrochemical charge storage devices such as battery and supercapacitor. On the other hand, the reversible optical modulation can be utilized for electrochromic (EC) application. However, the slow reaction kinetic of the redox reaction remains as a challenge and it has limited the rate capability of the oxide for both electrochemical devices.

In the present work, explorations in different modification on transition metal oxide have been carried out, aiming to enhance the two important prospective: capacitance and rate capability of the oxide. Modified transition metal oxides have been developed and applied as the electrode material for electrochromic (EC) device and supercapacitor. The oxide modifications are designed based on the electrochemical reaction mechanism and focus on three aspects: 1) oxide morphology and dimension, 2) metal ion insertion in the oxide and 3) oxide lattice structure. Significant enhancement in properties after these modifications have proven the effectiveness of these modifications and can be applied to the design of future transition metal oxide based electrode with high capacitance and good rate capability.

In this thesis, the effects of modifying oxide morphology and dimension have been evaluated by comparing the electrochemical and EC performances of non-porous and macroporous WO_3 film. It is found that there exist three criteria for a promising electrode. Firstly, oxide layer with interconnected pores is shown to be essential for the electrolyte penetration and the forming of oxide-electrolyte interface. The travel distance of the ion in the oxide lattice is effectively reduced by the penetration of electrolyte and hence the rate capability is improved. Secondly, large oxide-electrolyte interfacial area is preferred as it increases the reaction site for surface charge transfer process and the injection of ion into the oxide lattice. Both effects have enhanced the charge contribution from the electrochemical reaction and hence resulted in high capacitance. The last criterion is the nanometer scale oxide. The diffusion distance of the ion and hence the corresponding diffusion time has been found to be effectively reduced in the nanometer scale oxide, which helps to enhance the rate capability. Moreover, the whole oxide layer is more effectively utilized or even fully activated within short duration when the oxide layer is composed of nanometer scale oxide and well penetrated by the electrolyte. In this case, the material efficiency and specific capacitance (SC) are significantly enhanced.

A complete redox reaction in transition metal oxide requires the presence of electron and cation at the reaction site. The second part of the present work studied the effects of electronic conductivity and charge transfer rate on electrochemical reaction and charge storage performances from metal doping. Enhancement in electronic conductivity and charge transfer rate are observed after the metal doping and the surface dependent reaction has been promoted. This has in turn increased the SC of the oxide. It is also noted that the fast surface dependent reaction has been promoted after the doping and replacing the slow diffusion controlled reaction in the oxide. The

overall reaction is found to be dominated by the fast surface dependent reaction and the rate capability of the transition metal oxide has been enhanced.

Ion intercalation has been demonstrated to be another essential parameter for the redox reaction in transition metal oxide. In the process, the electrons are injected into the oxide to reduce the transition metal ions. In order to maintain the charge neutrality, cations are injected into the oxide lattice (through the oxide-electrolyte interface) and diffuse to the intercalation site adjacent to the reduced metal ion. Hence, the diffusion pathway and intercalation site, which are governed by the oxide lattice structure, are important for the ion intercalation process. In the last aspect of the present study, the effects of oxide lattice structure on electrochemical reaction and charge storage performances are investigated by comparing the performances of transition metal oxide with layered and framework lattice structure. It is found that the framework structure oxide, which possesses a tunnel as the fast diffusion pathway and three ion intercalation sites along the tunnel, exhibits better SC and rate capability than the layered structure oxide. These enhancements are attributed to the presence of tunnel in framework lattice, which has facilitated the diffusion controlled reaction. In addition, the easy accessible intercalation sites in the framework lattice have promoted both surface dependent and diffusion controlled reaction. The SC and rate capability are hence increased as higher amount of charge are stored in the oxide under the same scan rate.

In summary, designed strategies have been demonstrated in this thesis for the improvement in the capacitance and rate capability of transition metal oxide electrode. Oxide modifications, which specially designed based on the electrochemical reaction mechanism, have been shown to increase the total stored charge (i.e. the capacitance) and facilitate the surface dependent and diffusion controlled reaction in transition

metal oxide. The charge contribution from the electrochemical reactions can be increased through increasing the reaction site, enhancing the electron and ion transportation, and forming easy accessible intercalation site in the oxide. The rate capability in the oxide is also altered by these oxide modifications. With the promotion in surface dependent reaction after the oxide modifications, the overall reaction is dominated by this faster reaction and results in promising rate capability, which includes high capacitance retention and fast optical and electrochemical responses.

7.2 Recommendations for future work

7.2.1 Current collector and active material

The oxide electrodes demonstrated in this thesis are composed of a layer of nanostructured oxide (i.e. macroporous film or nanostructures) and conductive substrate (i.e. current collector). In another word, there is an interface created between the oxide and current collector. Several disadvantages could arise such as additional resistance occurs when the electrons pass this interface and the interface could be a weak link where the oxide starts to detach from the substrate. Additional works should be carried out on the current collector to further enhance the electrode performance. For example, the current collector can be a free standing nanowire array which can provide large surface area and connected pathway for electrolyte penetration. On the other hand, it is also possible to form a working electrode without current collector. For example of the V_2O_5 nanobelts demonstrate in Chapter 5 and 6, the long nanobelts can also be casted into a “paper like” film due to the entanglement among the nanobelts. This film can be directly used as the active material as well as the current collector with wire connects to it.

7.2.2 Redox peak in transition metal oxide

As shown in the cyclic voltammetry study of transition metal oxide, a large amount of capacitance contribution arises from the redox peaks. However, the redox peak is only occurring at a small voltage range. This means only small amount of charges is contributed from the rest of the voltage range and the maximum capacitance is only occurring at that small, specific voltage range. For actual application, composite

electrode could be employed to provide high current density and hence achieving high energy density. The composite electrode could compose of several kinds of active material, which can provide multiple redox peaks within the potential window of the device. Moreover, doping high level of additional transition metal ion into the oxide or forming binary or ternary oxide are also possible to produce additional redox peaks which correspond to redox reaction of different transition metal ion.

References

1. Wang, J.; Polleux, J.; Lim, J.; Dunn, B. *J. Phys. Chem. C* **2007**, 111, 14925-14931.
2. Khoo, E.; Wang, J.; Ma, J.; Lee, P. S. *J. Mater. Chem.* **2010**, 20, (38), 8368.
3. Frackowiak, E.; Beguin, F. *Carbon* **2001**, 39, (6), 937-950.
4. Conway, B. E., *Electrochemical supercapacitors : scientific fundamentals and technological applications* Kluwer Academic / Plenum Press: New York, 1999.
5. Pandolfo, A. G.; Hollenkamp, A. F. *J. Power Sources* **2006**, 157, (1), 11-27.
6. Conway, B. E.; Birss, V.; Wojtowicz, J. *J. Power Sources* **1997**, 66, (1-2), 1-14.
7. Simon, P.; Gogotsi, Y. *Nat. Mater.* **2008**, 7, (11), 845-854.
8. Sorensen, E. M.; Barry, S. J.; Jung, H. K.; Rondinelli, J. R.; Vaughey, J. T.; Poeppelmeier, K. R. *Chem. Mater.* **2006**, 18, (2), 482-489.
9. Wang, D.-W.; Fang, H.-T.; Li, F.; Chen, Z.-G.; Zhong, Q.-S.; Lu, G. Q.; Cheng, H.-M. *Adv. Funct. Mater.* **2008**, 18, (23), 3787-3793.
10. Jiang, C.; Zhou, Y.; Honma, I.; Kudo, T.; Zhou, H. *J. Power Sources* **2007**, 166, (2), 514-518.
11. Lindstrom, H.; Sodergren, S.; Solbrand, A.; Rensmo, H.; Hjelm, J.; Hagfeldt, A.; Lindquist, S.-E. *J. Phys. Chem. B* **1997**, 101, 7717-7722.
12. Lindstrom, H.; Sodergren, S.; Anita Solbrand; Rensmo, H.; Johan Hjelm; Hagfeldt, A.; Lindquist, S.-E. *J. Phys. Chem. B* **1997**, 101, 7717-7722.
13. Granqvist, C. G., *Handbook of Inorganic Electrochromic Materials*. Elsevier Science B.V.: Amsterdam, The Netherlands 1995.
14. Sapp, S. A.; Sotzing, G. A.; Reddinger, J. L.; Reynolds, J. R. *Adv. Mater.* **1996**, 8, (10), 808-811.
15. Bohnke, O.; Rousselot, C.; Gillet, P. A.; Truche, C. *J. Electrochem. Soc.* **1992**, 139, (7), 1862-1865.
16. Baeck, S. H.; Jaramillo, T. F.; Stucky, G. D.; McFarland, E. W. *Chem. Mater.* **2003**, 15, (18), 3411-3413.
17. Sasi, B.; Gopchandran, K. G. *Nanotech.* **2007**, 18, (11).
18. Cheng, W.; Baudrin, E.; Dunn, B.; Zink, J. I. *J. Mater. Chem.* **2001**, 11, (1), 92-97.
19. Khoo, E.; Wang, J. M.; Ma, J.; Lee, P. S. *J. Mater. Chem.* **2010**, 20, (38), 8368-8374.
20. Baeck, S. H.; Choi, K. S.; Jaramillo, T. F.; Stucky, G. D.; McFarland, E. W. *Adv. Mater.* **2003**, 15, (15), 1269-1273.
21. Hu, J.; Abdelsalam, M.; Bartlett, P.; Cole, R.; Sugawara, Y.; Baumberg, J.; Mahajan, S.; Denuault, G. *J. Mater. Chem.* **2009**, 19, (23), 3855-3858.
22. Li, L.; Steiner, U.; Mahajan, S. *J. Mater. Chem.* **2010**, 20, (34), 7131-7134.
23. Balaji, S.; Djaoued, Y.; Albert, A. S.; Ferguson, R. Z.; Bruning, R. *Chem. Mater.* **2009**, 21, (7), 1381-1389.
24. Deepa, M.; Srivastava, A. K.; Sood, K. N.; Agnihotry, S. A. *Nanotechnology* **2006**, 17, (10), 2625-2630.
25. Lee, S. H.; Deshpande, R.; Parilla, P. A.; Jones, K. M.; To, B.; Mahan, A. H.; Dillon, A. C. *Adv. Mater.* **2006**, 18, (6), 763-766.
26. Wang, J. M.; Khoo, E.; Lee, P. S.; Ma, J. *J. Phys. Chem. C* **2008**, 112, (37), 14306-14312.
27. Park, S. Y.; Lee, J. M.; Noh, C.; Son, S. U. *J. Mater. Chem.* **2009**, 19, (42), 7959-7964.

28. Wang, J. M.; Khoo, E.; Lee, P. S.; Ma, J. *J. Phys. Chem. C* **2009**, 113, (22), 9655-9658.
29. Zheng, L.; Xu, Y.; Jin, D.; Xie, Y. *Chem. Mater.* **2009**, 21, (23), 5681-5690.
30. Daothong, S.; Songmee, N.; Dejang, N.; Pichler, T.; Shiozawa, H.; Jia, Y.; Batchelor, D.; Kauppinen, E.; Thongtem, S.; Ayala, P.; Singjai, P. *J. Phys. Chem. C* **2010**, 114, (1), 10-14.
31. Hong, K. Q.; Yin, W. C.; Wu, H. S.; Gao, J.; Xie, M. H. *Nanotechnology* **2005**, 16, (9), 1608-1611.
32. Deepa, M. *Thin Solid Films* **2004**, 468, (1-2), 32-42.
33. Deepa, M.; Joshi, A. G.; Srivastava, A. K.; Shivaprasad, S. M.; Agnihotry, S. A. *J. Electrochem. Soc.* **2006**, 153, (5), C365.
34. Işık, D.; Ak, M.; Durucan, C. *Thin Solid Films* **2009**, 518, (1), 104-111.
35. Chen, Z.; Qin, Y. C.; Weng, D.; Xiao, Q. F.; Peng, Y. T.; Wang, X. L.; Li, H. X.; Wei, F.; Lu, Y. F. *Adv. Funct. Mater.* **2009**, 19, (21), 3420-3426.
36. Chen, Z.; Augustyn, V.; Wen, J.; Zhang, Y. W.; Shen, M. Q.; Dunn, B.; Lu, Y. F. *Adv. Mater.* **2011**, 23, (6), 791-+.
37. An, K. H.; Kim, W. S.; Park, Y. S.; Moon, J. M.; Bae, D. J.; Lim, S. C.; Lee, Y. S.; Lee, Y. H. *Adv. Funct. Mater.* **2001**, 11, (5), 387-392.
38. Frackowiak, E.; Beguin, F. *Carbon* **2002**, 40, (10), 1775-1787.
39. Frackowiak, E.; Metenier, K.; Bertagna, V.; Beguin, F. *Appl. Phys. Lett.* **2000**, 77, (15), 2421-2423.
40. An, K. H.; Kim, W. S.; Park, Y. S.; Choi, Y. C.; Lee, S. M.; Chung, D. C.; Bae, D. J.; Lim, S. C.; Lee, Y. H. *Adv. Mater.* **2001**, 13, (7), 497-+.
41. Gamby, J.; Taberna, P. L.; Simon, P.; Fauvarque, J. F.; Chesneau, M. *J. Power Sources* **2001**, 101, (1), 109-116.
42. Qu, D. Y. *J. Power Sources* **2002**, 109, (2), 403-411.
43. Xing, W.; Qiao, S. Z.; Ding, R. G.; Li, F.; Lu, G. Q.; Yan, Z. F.; Cheng, H. M. *Carbon* **2006**, 44, (2), 216-224.
44. Amarnath, C.; Chang, J.; Kim, D.; Mane, R.; Han, S.; Sohn, D. *Mater. Chem. Phys.* **2009**, 113, (1), 14-17.
45. Ismail, Y. A.; Chang, J.; Shin, S. R.; Mane, R. S.; Han, S.-H.; Kim, S. J. *J. Electrochem. Soc.* **2009**, 156, (4), A313.
46. Patra, S.; Munichandraiah, N. *J. Appl. Polym. Sci.* **2007**, 106, (2), 1160-1171.
47. Wang, J.; Xu, Y.; Chen, X.; Du, X. *J. Power Sources* **2007**, 163, (2), 1120-1125.
48. Sharma, R.; Rastogi, A.; Desu, S. *Electrochem. Commun.* **2008**, 10, (2), 268-272.
49. Suppes, G. M.; Deore, B. A.; Freund, M. S. *Langmuir* **2008**, 24, (3), 1064-1069.
50. Lin, Y. H.; Zhao, N. N.; Nie, W.; Ji, X. L. *J. Phys. Chem. C* **2008**, 112, (42), 16219-16224.
51. Zhang, J. T.; Ma, J. Z.; Zhang, L. L.; Guo, P. Z.; Jiang, J. W.; Zhao, X. S. *J. Phys. Chem. C* **2010**, 114, (32), 13608-13613.
52. Reddy, R. N.; Reddy, R. G. *J. Power Sources* **2006**, 156, (2), 700-704.
53. Lee, H. Y.; Goodenough, J. B. *J. Solid State Chem.* **1999**, 148, 81-84.
54. Wee, G.; Soh, H. Z.; Cheah, Y. L.; Mhaisalkar, S. G.; Srinivasan, M. *J. Mater. Chem.* **2010**, 20, (32), 6720.
55. Qu, Q. T.; Zhang, P.; Wang, B.; Chen, Y. H.; Tian, S.; Wu, Y. P.; Holze, R. *J. Phys. Chem. C* **2009**, 113, (31), 14020-14027.
56. Zhang, J. T.; Chu, W.; Jiang, J. W.; Zhao, X. S. *Nanotechnology* **2011**, 22, (12).
57. Zolfaghari, A.; Ataherian, F.; Ghaemi, M.; Gholami, A. *Electrochim. Acta* **2007**, 52, (8), 2806-2814.

58. Wei, T. Y.; Chen, C. H.; Chang, K. H.; Lu, S. Y.; Hu, C. C. *Chem.Mater.* **2009**, 21, (14), 3228-3233.
59. Prasad, K. R.; Koga, K.; Miura, N. *Chem.Mater.* **2004**, 16, (10), 1845-1847.
60. An, G. M.; Yu, P.; Xiao, M. J.; Liu, Z. M.; Miao, Z. J.; Ding, K. L.; Mao, L. Q. *Nanotechnology* **2008**, 19, (27).
61. Yu, C. C.; Zhang, L. X.; Shi, J. L.; Zhao, J. J.; Gao, J. H.; Yan, D. S. *Adv. Funct. Mater.* **2008**, 18, (10), 1544-1554.
62. Wang, H. Q.; Li, Z. S.; Huang, Y. G.; Li, Q. Y.; Wang, X. Y. *J. Mater. Chem.* **2010**, 20, (19), 3883-3889.
63. Zhang, H.; Cao, G. P.; Wang, Z. Y.; Yang, Y. S.; Shi, Z. J.; Gu, Z. N. *Nano Letters* **2008**, 8, (9), 2664-2668.
64. Yuan, C. Z.; Zhang, X. G.; Su, L. H.; Gao, B.; Shen, L. F. *J. Mater. Chem.* **2009**, 19, (32), 5772-5777.
65. Dong, X. P.; Shen, W. H.; Gu, J. L.; Xiong, L. M.; Zhu, Y. F.; Li, Z.; Shi, J. L. *J. Phys. Chem. B* **2006**, 110, (12), 6015-6019.
66. Sassoey, C.; Laberty, C.; Le Khanh, H.; Cassaignon, S.; Boissiere, C.; Antonietti, M.; Sanchez, C. *Adv. Funct. Mater.* **2009**, 19, (12), 1922-1929.
67. Susanti, D.; Tsai, D. S.; Huang, Y. S.; Korotcov, A.; Chung, W. H. *J. Phys. Chem. C* **2007**, 111, (26), 9530-9537.
68. Wu, Z. S.; Wang, D. W.; Ren, W.; Zhao, J.; Zhou, G.; Li, F.; Cheng, H. M. *Adv. Funct. Mater.* **2010**, 20, (20), 3595-3602.
69. Yuan, C. Z.; Chen, L.; Gao, B.; Su, L. H.; Zhang, X. G. *J. Mater. Chem.* **2009**, 19, (2), 246-252.
70. Patel, M. N.; Wang, X. Q.; Wilson, B.; Ferrer, D. A.; Dai, S.; Stevenson, K. J.; Johnston, K. P. *J. Mater. Chem.* **2010**, 20, (2), 390-398.
71. Chou, S.; Cheng, F.; Chen, J. *J. Power Sources* **2006**, 162, (1), 727-734.
72. Hu, C. C.; Wu, Y. T.; Chang, K. H. *Chem.Mater.* **2008**, 20, (9), 2890-2894.
73. Lin, C.; Ritter, J. A.; Popov, B. N. *J. Electrochem. Soc.* **1998**, 145, (12), 4097-4103.
74. Shinde, V. R.; Mahadik, S. B.; Gujar, T. P.; Lokhande, C. D. *Appl. Surf. Sci.* **2006**, 252, (20), 7487-7492.
75. Wang, G. X.; Shen, X. P.; Horvat, J.; Wang, B.; Liu, H.; Wexler, D.; Yao, J. *J. Phys. Chem. C* **2009**, 113, (11), 4357-4361.
76. Li, F. H.; Song, J. F.; Yang, H. F.; Gan, S. Y.; Zhang, Q. X.; Han, D. X.; Ivaska, A.; Niu, L. *Nanotechnology* **2009**, 20, (45).
77. Selvan, R. K.; Perelshtein, I.; Perkash, N.; Gedanken, A. *J. Phys. Chem. C* **2008**, 112, (6), 1825-1830.
78. Hu, C. C.; Chang, K. H.; Lin, M. C.; Wu, Y. T. *Nano Lett.* **2006**, 6, (12), 2690-2695.
79. Kim, J. H.; Zhu, K.; Yan, Y. F.; Perkins, C. L.; Frank, A. J. *Nano Lett.* **2010**, 10, (10), 4099-4104.
80. Salari, M.; Konstantinov, K.; Liu, H. K. *J. Mater. Chem.* **2011**, 21, (13), 5128-5133.
81. Fang, W. C. *J. Phys. Chem. C* **2008**, 112, (30), 11552-11555.
82. Liu, J.; Wang, X.; Peng, Q.; Li, Y. *Adv. Mater.* **2005**, 17, (6), 764-767.
83. Coustier, F.; Hill, J.; Owens, B. B.; Passerini, S.; Smyrl, W. H. *J. Electrochem. Soc.* **1999**, 146, (4), 1355-1360.
84. Coustier, F.; Passerini, S.; Smyrl, W. H. *Solid State Ionics* **1997**, 100, 247-258.
85. Gies, A.; Pecquenard, B.; Benayad, A.; Martinez, H.; Gonbeau, D.; Fuess, H.; Levasseur, A. *Thin Solid Films* **2008**, 516, (21), 7271-7281.

86. Shim, S. E.; Cha, Y. J.; Byun, J. M.; Choe, S. *J. Appl. Polym. Sci.* **1999**, 71, (13), 2259-2269.
87. Meulenkaamp, E. A. *J. Electrochem. Soc.* **1997**, 144, (5), 1664-1671.
88. Niklasson, G. A.; Granqvist, C. G. *J. Mater. Chem.* **2007**, 17, (2), 127.
89. Granqvist, C. G. *Sol. Energy Mater. Sol. Cells* **2000**, 60, 201-262.
90. Greenberg, C. B. *Thin Solid Films* **1994**, 251, (2), 81-93.
91. Lampert, C. M. *Sol. Energy Mater. Sol. Cells* **2003**, 76, 489-499.
92. Lee, S.-H.; Cheong, H. M.; Tracy, C. E.; Mascarenhas, A.; Pitts, J. R.; Jorgensen, G.; Deb, S. K. *Appl. Phys. Lett.* **2000**, 76, (26), 3908-3910.
93. Leftheriotis, G.; Yianoulis, P. *Solid State Ionics* **2008**, 179, (38), 2192-2197.
94. Baek, S.-H.; Choi, K.-S.; Jaramillo, T. F.; Stucky, G. D.; McFarland, E. W. *Adv. Mater.* **2003**, 15, (15), 1269-1273.
95. Hsu, C. S.; Lin, C. K.; Chan, C. C.; Chang, C. C.; Tsay, C. Y. *Thin Solid Films* **2006**, 494, (1-2), 228-233.
96. Jiang, F. S.; Zheng, T.; Yang, Y. *J. Non-Cryst. Solids* **2008**, 354, (12-13), 1290-1293.
97. Sallard, S.; Brezesinski, T.; Smarsly, B. M. *J. Phys. Chem. C* **2007**, 111, (19), 7200-7206.
98. Zhang, J.; Wang, X. L.; Xia, X. H.; Gu, C. D.; Zhao, Z. J.; Tu, J. P. *Electrochim. Acta* **2010**, 55, (23), 6953-6958.
99. Deepa, M.; Srivastava, A.; Agnihotry, S. *Acta Materialia* **2006**, 54, (17), 4583-4595.
100. Liao, C.; Chen, F.; Kai, J. *Sol. Energy Mater. Sol. Cells* **2006**, 90, (7-8), 1147-1155.
101. Denesuk, M.; Uhlmann, D. R. *J. Electrochem. Soc.* **1996**, 143, (9), L186-L188.
102. Wen, C. J.; Boukamp, B. A.; Huggins, R. A.; Weppner, W. *J. Electrochem. Soc.* **1979**, 126, (12), 2258-2266.
103. Levi, M. D.; Aurbach, D. *Electrochim. Acta* **1999**, 45, 167-185.
104. Montella, C. *J. Electroanal. Chem.* **2002**, 518, 61-83.
105. Driel, F. v.; Decker, F.; Simone, F.; Pennisi, A. *J. Electroanal. Chem.* **2002**, 537, 125-134.
106. Levi, M. D.; Levi, E. A.; Aurbach, D. *J. Electroanal. Chem.* **1997**, 421, 89-97.
107. Vertes, A.; Schiller, R. *J. Appl. Phys.* **1983**, 54, 199-203.
108. Zhang, J.-G.; Tracy, C. E.; Benson, D. K.; Deb, S. K. *J. Mater. Res.* **1993**, 8, (10), 2649-2656.
109. Habib, M. A.; Glueck, D. *Sol. Energy Mater. Sol. Cells* **1989**, 18, 127-141.
110. Crandall, R. S.; Faughnan, B. W. *Appl. Phys. Lett.* **1976**, 28, (2), 95-97.
111. Gre goire, G.; Baffier, N.; Kahn-Harari, A. e.; Badot, J.-C. *J. Mater. Chem.* **1998**, 8, (9), 2103-2108.
112. Wei, Y.; Ryu, C.; Kim, K. *J. Alloys Compd.* **2008**, 459, (1-2), L13-L17.
113. Podval'naya, N. V.; Bakhteeva, Y. A. *Inorg. Mater.* **2010**, 46, (1), 47-50.
114. Delmas, C.; Cognac-Auradou, H.; Cocciantelli, J. M.; Menetder, M.; Doumerc, J. P. *Solid State Ionics* **1994**, 69, 257-164.
115. Hwang, H.; Oh, S.; Kim, H.; Cho, W.; Cho, B.; Lee, D. *Electrochim. Acta* **2004**, 50, (2-3), 485-489.
116. Xiong, C.; Aliev, A. E.; Gnade, B.; Kenneth J. Balkus, J. *ACS Nano* **2008**, 2, (2), 293-301.
117. Jiao, L. F.; Yuan, H. T.; Si, Y. C.; Wang, Y. J.; Wang, Y. M. *Electrochem. Commun.* **2006**, 8, (6), 1041-1044.

118. Coustier, F.; Jarero, G.; Passerini, S.; Smyrl, W. H. *J. Power Sources* **1999**, 83, (1-2), 9-14.
119. Wei, Y. J.; Ryu, C. W.; Kim, K. B. *J. Alloy. Compd.* **2008**, 459, (1-2), L13-L17.
120. Park, H. K. *Solid State Ion.* **2005**, 176, (3-4), 307-312.
121. Yu, D. M.; Zhang, S. T.; Liu, D. W.; Zhou, X. Y.; Xie, S. H.; Zhang, Q. F.; Liu, Y. Y.; Cao, G. Z. *J. Mater. Chem.* **2010**, 20, (48), 10841-10846.
122. Li, Y. M.; Hibino, M.; Tanaka, Y.; Wada, Y.; Noguchi, Y.; Takano, S.; Kudo, T. *Solid State Ion.* **2001**, 143, (1), 67-72.
123. Enyashin, A. N.; Ivanovskaya, V. V.; Makurin, Y. N.; Volkov, V. L.; Ivanovskii, A. L. *Chem. Phys. Lett.* **2004**, 392, (4-6), 555-560.
124. Mai, L. Q.; Chen, W.; Xu, Q.; Peng, J. F.; Zhu, Q. Y. *Chem. Phys. Lett.* **2003**, 382, (3-4), 307-312.
125. Song, J.-M.; Lin, Y.-Z.; Yao, H.-B.; Fan, F.-J.; Li, X.-G.; Yu, S.-H. *ACS Nano* **2009**, 3, (3), 653-660.
126. Shao, M.-W.; Lu, L.; Wang, H.; Wang, S.; Zhang, M.-L.; Ma, D.-D.-D.; Lee, S.-T. *Chem. Commun.* **2008**, 20, (20), 2310.
127. Li, M.; Shao, M.; Ban, H.; Wang, H.; Gao, H. *Solid State Ionics* **2007**, 178, (11-12), 775-777.
128. Chen, Z.; Qin, Y.; Weng, D.; Xiao, Q.; Peng, Y.; Wang, X.; Li, H.; Wei, F.; Lu, Y. *Adv. Funct. Mater.* **2009**, 19, (21), 3420-3426.
129. Qu, Q. T.; Shi, Y.; Li, L. L.; Guo, W. L.; Wu, Y. P.; Zhang, H. P.; Guan, S. Y.; Holze, R. *Electrochem. Commun.* **2009**, 11, (6), 1325-1328.
130. Huang, C. M.; Hu, C. C.; Chang, K. H.; Li, J. M.; Li, Y. F. *J. Electrochem. Soc.* **2009**, 156, (8), A667-A671.
131. Moulder, J. F., *Handbook of x-ray photoelectron spectroscopy : a reference book of standard spectra for identification and interpretation of XPS data* Physical Electronics: Eden Prairie, Minn., 1995.
132. Passerini, S.; Le, D. B.; Smyrl, W. H.; Berrettoni, M.; Tossici, R.; Marassi, R.; Giorgetti, M. *Solid State Ionics* **1997**, 104, 195-204.
133. Bensch, W.; Worner, E.; Muhler, M. *Mater. Res. Bull.* **1994**, 29, (2), 155-166.
134. Wark, M.; Koch, M.; Bruckner, A.; Grunert, W. *J. Chem. Soc. Faraday Trans.* **1998**, 94, (14), 2033-2041.
135. Silversmit, G.; Depla, D.; Poelman, H.; Marin, G. B.; De Gryse, R. *J. Electron Spectrosc. Relat. Phenom.* **2004**, 135, (2-3), 167-175.
136. Takami, H.; Kanki, T.; Ueda, S.; Kobayashi, K.; Tanaka, H. *Appl. Phys. Express* **2010**, 3, (6).
137. Zimmermann, R.; Claessen, R.; Reinert, F.; Steiner, P.; Hufner, S. *J. Phys.-Condes. Matter* **1998**, 10, (25), 5697-5716.
138. Nordlinder, S.; Augustsson, A.; Schmitt, T.; Guo, J.; Duda, L. C.; Nordgren, J.; Gustafsson, T. r.; Edstro'm, K. *Chem.Mater.* **2003**, 15, (16), 3227-3232.
139. Bard, A. J.; Faulkner, L. R., *Electrochemical Methods: Fundamentals and Application*. John Wiley and Sons: New York, 1980.
140. Brezesinski, T.; Wang, J.; Senter, R.; Brezesinski, K.; Dunn, B.; Tolbert, S. H. *ACS Nano* **2010**, 4, (2), 967-977.
141. Brezesinski, T.; Wang, J.; Polleux, J.; Dunn, B.; Tolbert, S. H. *J. Am. Chem. Soc.* **2009**, 131, (5), 1802-1809.
142. Brezesinski, T.; Wang, J.; Tolbert, S. H.; Dunn, B. *Nat. Mater.* **2010**, 9, (2), 146-151.
143. Sze, S. M., *Semiconductor devices, physics and technology* Wiley: New York, 2002.

144. Bandyopadhyay, S.; Paul, G. K.; Roy, R.; Sen, S. K.; Sen, S. *Mater. Chem. Phys.* **2002**, 74, (1), 83-91.
145. Dhage, S. R.; Samuel, V.; Ravi, V. *J. Electroceram.* **2003**, 11, (1-2), 81-87.
146. Yamamoto, T.; Suzuki, S.; Kawaguchi, K.; Takahashi, K. *Jpn. J. Appl. Phys. Part 1 - Regul. Pap. Short Notes Rev. Pap.* **1998**, 37, (9A), 4737-4746.
147. Jayalakshmi, M.; Rao, M. M.; Venugopal, N.; Kim, K. B. *J. Power Sources* **2007**, 166, (2), 578-583.
148. Ghodbane, O.; Pascal, J.-L.; Favier, F. *ECS Transactions* **2008**, 16, 235-241.
149. Brousse, T.; Toupin, M.; Dugas, R.; Athouël, L.; Crosnier, O.; Bélanger, D. *J. Electrochem. Soc.* **2006**, 153, (12), A2171.
150. Galy, J. *J. Solid State Chem.* **1992**, 100, 229-245.
151. Galy, J.; Darriet, J.; Casalot, A.; Goodenough, J. B. *J. Solid State Chem.* **1970**, 1, 339-348.
152. Yang, Y.; Zhu, Q.; Jin, A.; Chen, W. *Solid State Ionics* **2008**, 179, (21-26), 1250-1255.
153. West, K.; Zachau-Christianse, B.; Jacobsen, T.; Skaarup, S. *Electrochim. Acta* **1993**, 39, 1215-1220.
154. Wu, W. Z.; Ding, J.; Peng, H. R.; Li, G. C. *Mater. Lett.* **2011**, 65, (14), 2155-2157.
155. Rozier, P.; Galy, J. *J. Solid State Chem.* **1997**, 134, (2), 294-301.
156. Kumagai, N.; Yu, A.; West, K. *J. Appl. Electrochem.* **1997**, 27, (8), 953-958.
157. Bach, S.; Baffier, N.; Pereira-Ramos, J. P.; Messina, R. *Solid State Ionics* **1989**, 37, 41-49.
158. Bach, S.; Pereira-Ramos, J. P.; Baffler, N.; Messina, R. *J. Electrochem. Soc.* **1990**, 137, 1042-1048.
159. Reddy, R. *J. Power Sources* **2006**, 156, (2), 700-704.