

Sputtered Vanadium-based Cathode for Zinc Ion Battery

BY

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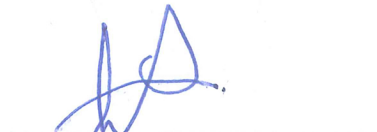


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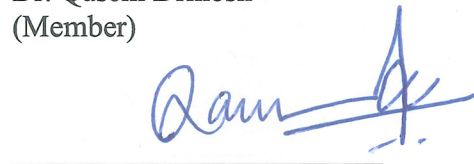
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DEDICATED TO

MY BELOVED PARENTS, WIFE AND DAUGHTER

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TABLE OF CONTENTS

ACKNOWLEDGEMENT	iv
LIST OF CONTENTS	v
LIST OF TABLES	vii
LIST OF FIGURES	viii
THESIS ABSTRACT (ENGLISH).....	x
THESIS ABSTRACT (ARABIC)	xii
Chapter 1: Introduction	1
1.1 Introduction.....	1
1.2 Zinc Ion Batteries.....	3
1.2.1 Cathode Materials for ZIB.....	5
1.2.2 Charge Storage Mechanism in ZIBs	8
Chapter 2: Literature Review	12
2.1 Vanadium Oxide Cathode Thin Films	18
2.2 Challenges for Vanadium Oxide.....	18
2.3 Thin Film Sputtering	21
2.4 Role of Annealing on Sputtering.....	26
2.5 Objectives.....	28
Chapter 3: Experimental Procedure	29
3.1 Fabrication of Coin cell	29
3.2 Material Synthesis.....	31
3.3 Material Characterization Techniques	32
3.4 Electrochemical Characterization techniques.....	32
Chapter 4: Results and Discussion	34
4.1 Crystallographic and Microstructural Analysis	34
4.1.1 X-Ray Diffraction (XRD)	34
4.1.2 Scanning Electron Microscope (SEM)	39
4.1.3 Optical Profilometry	42
4.2 Electrochemical Results.....	43

4.2.1 Cyclic Voltammetry	43
4.2.2 Galvanostatic Charging Discharging (GCD).....	46
4.2.3 Electrochemical Impedance Spectroscopy (EIS).....	49
4.2.4 Discharge Specific Capacity	50
4.2.5 Degradation Mechanism.....	51
Chapter 5: Conclusion	54
5.1 Conclusion	54
5.2 Future Recommendations	55
References.....	57
Vitae	

LIST OF TABLES

Table 1: shows comparison of different parameters such as ionic radius, atomic weight, Specific capacity, energy density and cost for different energy storage materials [3]	3
Table 2: Electrochemical performance of different vanadium-based oxide materials for ZIBs	15
Table 3: Sample details such as deposition time, oxygen ratio and thin film thickness.....	23
Table 4: Sputtering parameters such as deposition time and layer thickness for vanadium oxide.	42

LIST OF FIGURES

Figure 1: Comparison of properties such as specific gravimetric and volumetric capacity, cation radius and potential (vs SHE) for rechargeable aqueous electrolyte-based batteries [5].....	2
Figure 2: Comparison for specific capacities for different materials and oxides [12]......	5
Figure 3: Different strategies to improve the performance of cathode materials in ZIBs [15]......	7
Figure 4: ZIB structure along with the potential candidates for cathode materials [17]......	8
Figure 5: Pie-chart representing the ratio of publication of different energy storage materials [8]......	8
Figure 6: General Energy storage mechanism for Zn-ion battery [12]......	9
Figure 7: Different charge storage mechanisms for ZIBs [19].	10
Figure 8: Zn^{2+} ion intercalation and de-intercalation process [30].	13
Figure 9: Graphical representation of intercalation/de-intercalation process for Zn ion during charging and discharging process [3].	14
Figure 10: Graphical representation of $\text{Zn}/\text{Zn}_{0.25}\text{V}_2\text{O}_5$ cell [3].	15
Figure 11: Intercalation and deintercalation of Al ion in tunnel structure of VO_2 [48].	17
Figure 12: Tunnel single phase structure of VO_2 cathode during charging and discharging process [21].	18
Figure 13: Issues and limitation of ZIBs with aqueous electrolyte [55].	20
Figure 14: Schematic of DC Sputtering [61].	22
Figure 15: Raman Spectra of different vanadium oxide samples with variable oxygen ratio [64]......	24
Figure 16: SEM images for vanadium oxide thin film surfaces [65]......	25
Figure 17: XRD spectra of vanadium oxide samples [65]......	25
Figure 18: XRD spectra of annealed or oxidized vanadium oxide [67].	27
Figure 19: XPS spectra of vanadium oxide films [63]......	27
Figure 20: General schematics for fabrication of a coin cell battery.	29
Figure 21: Pressure controlled crimper used for coin cell fabrication.	30
Figure 22: Disc cutting machine for coin cell fabrication.	30
Figure 23: Sputtering setup for the fabrication of VO cathode material.....	31
Figure 24: Flow-chart of this research study	33
Figure 25: XRD pattern of Ti foil substrate, reference V_2O_5 , 0.5 micron and 1 micron Vanadium Oxide prepared by post-annealing treatment of sputtered V thin films at 600 °C	36
Figure 26: XRD pattern for Ti foil substrate, reference V_2O_5 , Vanadium oxide prepared by post-annealing treatment of sputtered V thin films at 200 °C, 400 °C and 600 °C.	37
Figure 27: XRD pattern for Ti foil substrate, reference V_2O_5 , 1-micron thin film with annealing at 600 °C, and sputtering with oxygen gas (approach 2).	38

Figure 28: SEM images of two-dimensional (2D) layered of Vanadium oxides microflakes (2 μm V, 600 $^{\circ}\text{C}$) at two different magnification (a) 10,000 and (b) 2,500	40
Figure 29: SEM images of two-dimensional (2D) layered of Vanadium oxides microflakes (1 μm V, 600 $^{\circ}\text{C}$) at two different magnification (a) 10,000 and (b) 2,500	41
Figure 30: SEM images of two-dimensional (2D) layered Vanadium oxides thin film (AS deposited V, post-annealed at 200 $^{\circ}\text{C}$ and post-annealed at 600 $^{\circ}\text{C}$).	41
Figure 31: SEM images of two-dimensional (2D) layered vanadium oxides thin film (Sputtered with O_2) at two different magnification (a) 10,000 and (b) 2,500	41
Figure 32: Optical Profilometry for sputtered Vanadium.	42
Figure 33: CV curves of V_2O_5 with different thickness of metal layer (approach 1), compared to sputtered with Oxygen (approach2) Scan rate 10 mV/S	44
Figure 34: CV curves of V_2O_5 with different thickness of metal layer (approach 1), compared to sputtered with Oxygen (approach2). Scan rate 100 mV/S	45
Figure 35: CV curves for annealed thin films at 200, 400 and 600 $^{\circ}\text{C}$ at scan rate of 10 mV/s for the optimized condition (1 μm , approach1).....	45
Figure 36: CV voltammogram for Vanadium oxide thin film at different scan rates. For the optimized condition (1 μm , 600 $^{\circ}\text{C}$)	46
Figure 37: GCD analysis for Vanadium oxide thin film at different current densities. For the optimized condition (1 μm , 600 $^{\circ}\text{C}$)	47
Figure 38: GCD analysis for Vanadium oxide post annealed at different temperature.	48
Figure 39: GCD analysis of Vanadium oxide with thickness of 0.5 and 1 microns at the optimized temperature (600 $^{\circ}\text{C}$) and as-sputtered with O_2 gas (blue)	48
Figure 40: EIS of optimized condition of Vanadium Oxide before and after 500 charge/discharge cycles.	49
Figure 41: Discharge Specific Capacity for annealed samples of 0.5 and 1 micron and oxygen sputtered samples.....	50
Figure 42: Degradation and material transfer of cathode material to anode.....	51
Figure 43: XRD pattern for Zn foil before and after 500 cycles.....	52
Figure 44: XRD pattern for Ti foil substrate, V_2O_5 at 600 $^{\circ}\text{C}$ annealing after 500 cycles.	53

THESIS ABSTRACT (ENGLISH)

NAME: Ramzi AlMaghthawi

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Fossil fuels are the main source of energy in the world. More than 80 % of energy is produced through these sources that have severe environmental impact and emit harmful greenhouse gases. To meet the energy demands and to overcome the issues with global warming, there is a growing need for renewable energy sources, but the intermittency issues with these sources require reliable energy storage systems. Lithium-ion Batteries (LIBs) are being widely used for energy storage, but there are certain disadvantages such as cost, safety issues, and limited availability of lithium. Green, affordable, and safe energy storage systems are required to meet rising energy demands and mitigate the harmful environmental effects of increased energy usage. Therefore, new battery technologies such as Zinc-ion batteries (ZIBs) have gained attraction due to safer, ecofriendly, and cost-effective energy storage solutions. Compared to other multivalent ionic energy storage batteries, ZIBs employ aqueous electrolytes. To achieve sustainable growth in employing renewable energy and energy storage systems, innovative aqueous ZIBs are seen as the most promising alternatives. The cathode material of ZIB plays a very critical role in enhancing energy storage capabilities via efficient insertion and extraction of Zinc ions. ZIBs have certain advantages such as high theoretical capacity, high electric conductivity, high energy density, low redox potential, abundance of raw materials, economic feasibility, recyclability, and scalability. Cathode materials are the main hinderance and bottleneck in the commercialization and advance applications of ZIBs. Suitable thin film cathode materials need reversible charge storage mechanism along with higher charge and voltage capacity. Moreover, cathode materials require high structural integrity and stability to ensure performance during charging and discharging cycles. Vanadium oxide is a potential candidate for cathode material due to its high theoretical capacity and good cycling stability. To fabricate thin films of Vanadium oxide cathode materials, two methods are proposed for this study that include DC sputtering followed by post-annealing

treatment and DC sputtering with oxygen partial pressure. Microstructural and electrochemical analysis showed that the performance of Vanadium-based thin films was influenced by factors such as annealing temperature and film thickness. The XRD analysis reveals the presence of main diffraction peaks for monolithic and crystalline V_2O_5 phase demonstrating the successful formation of oxidized layer. Cyclic voltammetry analysis revealed the electrochemical behavior of the cathodes, showing characteristic oxidation and reduction peaks. Discharge-specific capacity tests exhibited the charge storage capacity of the cathodes. Electrochemical impedance spectroscopy analyzed the resistance of the thin film cathodes while associating them with performance and efficiency.

Galvanostatic charge-discharge analysis showed the charging and discharging behavior of the cathodes, indicating their reversible charge storage mechanism. Vanadium-based thin film cathodes showed good cycling stability and maintained their performance over repeated charge-discharge cycles. However, during the 500 cycles testing, a decrease in the performance of the cathodes was observed, likely attributed to degradation and a collapse in the 2-D structure resulted from processing Vanadium oxide thin films. Future research should focus on enhancement to the Zinc Anode by a passivation layer to reduce dendrite formation. In addition, and since choice of electrolyte is important, solid-state electrolyte should be considered. Approaches of 3D processing of the cathode within the current collector foam or mesh-like configuration is proven to result in a better electrochemical performance with other tested cathode materials and should be investigated.

THESIS ABSTRACT (ARABIC)

الاسم: رمزي المغنوي

عنوان الرسالة: تحضير كاثود من أكسيد الفاناديوم بعملية التغطية برش الجزيئات لاستخدامها في بطارية الزنك

التخصص: علوم وهندسة المواد

التاريخ: أغسطس - 2023

الوقود الأحفوري هو المصدر الرئيسي للطاقة في العالم. حيث يتم إنتاج أكثر من 80% من الطاقة من خلال هذه المصادر التي لها تأثير بيئي ضار. لذلك هناك حاجة متزايدة لمصادر الطاقة المتجددة، لتلبية متطلبات الطاقة والتغلب على مشكلات الاحتباس الحراري، لكن الاستمرارية مع هذه المصادر تتطلب أنظمة تخزين طاقة موثوقة.

تُستخدم بطاريات الليثيوم على نطاق واسع لتخزين الطاقة، ولكن من عيوبها، التكلفة و السلامة وقلة توافر الليثيوم. يُنظر إلى بطاريات الزنك على أنها أكثر البدائل الواعدة لتحقيق نمو مستدام في الطاقة المتجددة وأنظمة التخزين. تلعب مادة الكاثود في بطارية الزنك دورًا مهمًا في تعزيز قدرات تخزين الطاقة من خلال إدراج واستخراج أيونات الزنك بكفاءة عالية. تتمتع بطاريات الزنك بمزايا قوية مثل السعة النظرية والموصلية الكهربائية العالية وكثافة الطاقة العالية وإمكانية الأكسدة المنخفضة ووفرة المواد الخام والجدوى الاقتصادية.

يعتبر دور الكاثود هو العائق الرئيسي أمام التطبيقات لبطاريات الزنك. حيث تحتاج مواد الكاثود ذات السماكة الرقيقة إلى آلية تخزين شحنة عكسية إلى جانب سعة شحن وجهد أعلى. كما تتطلب مواد الكاثود سلامة هيكلية عالية واستقرارًا لضمان الأداء العالي. أيضًا، أكسيد الفاناديوم هو مادة مرشحة بدور الكاثود نظرًا لقدرته النظرية العالية واستقراره الجيد أثناء دورة العمل. وبهدف تصنيع طبقات ذات سماكة منخفضة من أكسيد الفاناديوم، في هذه الدراسة تم اقتراح طريقتين تتضمن تحضير أكسيد الفاناديوم برش جزيئات المادة في حجرة في بيئة ضغط شبه معدوم بتيار كهربائي مستمر متبوعًا بمعالجة حرارية والطريقة الأخرى باستخدام غاز الأكسجين لتمكين الأكسدة داخل الحجرة أثناء رش الجزيئات.

أظهر تحليل البنية المجهرية والكهروكيميائية أن أداء هذه الطبقات الرقيقة القائمة على الفاناديوم التي تم تطويرها في هذه الدراسة قد تأثر بدرجة الحرارة وسمك الغشاء. يكشف تحليل دراسة البلورات بالأشعة السينية عن وجود قمم الحيود الرئيسية لمرحلة أكسيد الفاناديوم الخماسي. المتجانسة مما يدل على التكوين الناجح للطبقة المؤكسدة. كشف تحليل الفولتميتر الدوري عن السلوك الكهروكيميائي للكاثودات، حيث أظهر الأكسدة في التفاعل داخل البطارية

يجب أن تركز الأبحاث المستقبلية على تحسين أنود الزنك بطبقة التخميل (كبت الفاعلية) لتقليل تشكل التشعبات. بالإضافة إلى ذلك، وحيث أن اختيار الإلكتروليت مهم، ينبغي النظر في إلكتروليت من الحالة الصلبة. فقد ثبت أن التجهيز الثلاثي الأبعاد للكاثود داخل البطارية من هذا النوع يؤدي إلى أداء كهروكيميائي أفضل مع مواد الكاثود الأخرى التي تم اختبارها ولذلك يجب فحصها.

Chapter 1: Introduction

1.1 Introduction

More than 80% of the world energy needs are met by electricity produced from environmentally harmful fossil fuels. Fossil fuels are predicted to last for just a few more decades due to the latest geographical issues and limited reserves. It is estimated that the population of the world would rise to 9.7 billion and the energy consumption will exceed 1000 exajoule by 2050 [2]. High CO₂ emissions from fossil fuel-based electricity are causing extreme environmental pollution and issues like global warming. The best solution to this climate crisis is to replace fossil fuels with more eco-friendly energy sources and energy storage systems. The need for renewable energy, free of harmful emissions, is increasing exponentially due to ever-increasing issues of global warming, climate change and greenhouse gases emissions. Renewable energy requires high performance and efficient energy storage systems due to the unpredictable nature of renewable energy harvesting and to cater for the ever-increasing energy demands [1]. Factors such as high energy density, compact size and higher cyclic performance make Li-ion batteries the most preferred energy storage systems. Lithium-ion batteries (LIBs) are believed to be the gateway for carbon-free energy storage, making them the most preferred technology for various applications. However, the practical applications of Li-ion batteries are limited because of higher costs, safety concerns and a very limited supply of lithium. These limitations hinder wide-scale applications of Li-ion batteries to integrate in power grids and heavy industrial units [2]. These limitations bring attention towards better alternatives such as Zinc-ion batteries (ZIBs) that are better alternative to LIBs mainly because of the abundance of raw materials, economic feasibility, enhanced safety, eco-friendliness, low redox potential, high cyclic stability, and low costs [3].

Development of new materials is making it possible to achieve high energy density and low-cost batteries for large-scale energy storage systems. Due to high safety and environmental beneficial characteristics, aqueous Na and Li-ion batteries are being investigated and researched to meet future energy demands. But these aqueous Na and Li batteries are facing issues with electrodes having low energy storage capacities of around 150 mAhg⁻¹, which limits the potential applications [6]. Even with these shortcomings, aqueous electrolyte batteries are considered much safer and economical that are easy to fabricate and can have higher ionic conductivity up to 1000 mS/cm while non-aqueous or organic electrolyte batteries have lower

ionic conductivities (up to 10 mS/cm). Following up to the need of green energy solutions and batteries that perform better in terms of energy density, power, safety and cost, the use of multivalent cation such as Al^{3+} , Zn^{2+} , Ca^{2+} , Ni^{2+} in aqueous batteries is the pathway to accomplish the green energy goals. Due to these significant advantages, considerable attention is being given to aqueous electrolyte and multivalent ZIBs [4]. High theoretical capacity, high electric conductivity, high energy density, low redox potential, abundance of raw materials, economic feasibility, recyclability and scalability are some of the advantages associated with ZIBs. Figure 1 shows the comparison of specific gravimetric and volumetric capacity, cation radius and potential (vs SHE) for different multivalent cations used for rechargeable aqueous electrolyte-based batteries [5].

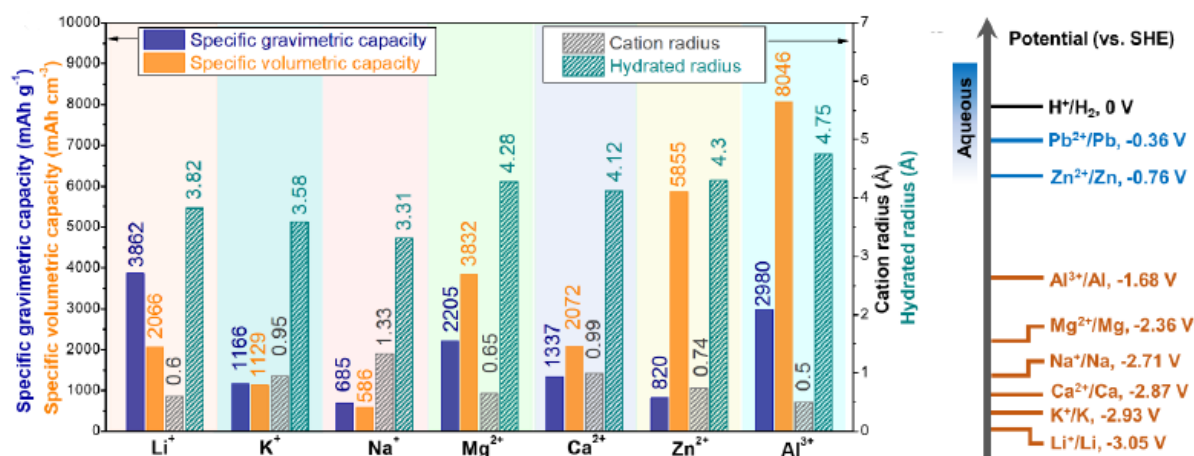


Figure 1: Comparison of properties such as specific gravimetric and volumetric capacity, cation radius and potential (vs SHE) for rechargeable aqueous electrolyte-based batteries [5].

ZIBs show reasonable performance when compared to other multi valent ion batteries as shown in figure 1 and have potential to improve the performance significantly but still ZIBs are far from being used in high end and advanced energy applications. The main hinderance in commercialization and advance applications is the cathode material used in ZIBs. Suitable cathode materials need reversible charge storage mechanism along with higher charge and voltage capacity. Moreover, cathode materials require high structural integrity and stability to ensure the performance during charging and discharging cycles. The cathode materials must be selected carefully, keeping in mind the applications of ZIBs [6].

1.2 Zinc Ion Batteries

Zinc is abundantly available as a natural source with a concentration of 79 ppm [7]. Zinc is the fourth most produced/mined material on earth. The advantages of Zn include the economic feasibility, high electrical conductivity of $5.91 \mu\Omega\text{cm}$, specific capacity of 819 mAh/g , energy density of 5851 mAh/cm^3 , and significantly low redox potential (E) (-0.76 V Vs SHE) [7]. These advantages make Zinc better suited for aqueous electrolytes. In comparison with univalent batteries, multivalent zinc ions can give two electrons, leading to more energy storage capacity. Zinc ions have radius of $0.74 \text{ \AA}$, which is close to that of lithium ions ($0.69 \text{ \AA}$) and less than that of sodium ions ($1.02 \text{ \AA}$) making it a great candidate for energy storage devices [7]. In short, Zn offers advantages over other materials due to its inexpensive, non-toxic nature, abundant supply, simple recycling, and low environmental impact. Table 1 shows comparison of different parameters such as ionic radius, atomic weight, specific capacity, energy density and cost for different energy storage materials [8]. Figure 2 shows the comparison of specific capacities for different materials.

Table 1: Comparison of different parameters such as ionic radius, atomic weight, Specific capacity, energy density and cost for different energy storage materials [8].

Element	Na ⁺	Li ⁺	Mg ²⁺	K ⁺	Ca ²⁺	Al ³⁺	Zn ²⁺
Atomic Weight (g/mol)	22.99	6.94	24.31	39.10	40.08	26.68	65.38
Ionic Radius (Å)	1.02	0.76	0.72	1.38	1.0	0.535	0.75
Gravimetric Capacity or specific capacity (mAh/g)	685	3862	2205	1166	1337	2980	820

Volumetric Capacity or Energy Density (mAh/cm ³)	585	2066	3832	1129	2072	8046	5855
Density (g/cm ³)	0.9	0.53	1.74	0.89	1.55	2.7	7.13
Cost (USD/kg)	3.1	19.2	2.2	13.1	-	1.9	2.2
Standard potential (E) Vs SHE	-2.71	-3.04	-2.37	-2.93	-2.87	-1.66	-0.76

Aqueous electrolytes have better ionic safety and conductivity as the ionic conductivities of aqueous electrolytes are more than two folds of magnitude than those of organic electrolytes. Aqueous batteries often have higher power densities. Aqueous electrolytes are harmless and safe, in contrast to the poisonous and combustible nature of organic electrolytes [9]. These aqueous electrolytes can minimize the environmental impact and lower recycling expenses. It is possible to assemble ZIBs under ambient conditions due to the high stability of zinc-based anode material and aqueous electrolyte. The production costs of ZIBs are significantly lower than other batteries that require inert-gas environment and use of glove box. The simple manufacturing process of ZIBs and relative ease of recycling is a significant benefit for large and industrial-scale storage units [10].

As metallic zinc-based anodes exhibit low redox potential of around -0.76 V vs. standard hydrogen electrode, preferable Zn/Zn²⁺ reverse ability in aqueous electrolytes, higher capacity of around 820 mAhg⁻¹, more interests are being shown to exploit Zn²⁺ storage chemistry by using aqueous electrolytes has recently attracted increasing interest. However, there are still significant limitations to the development and research of aqueous ZIBs, primarily in selecting and further designing of suitable cathode materials that are compatible with ZIBs. Vanadium based

oxides, manganese oxides, prussian blue analogues, polyanion and quinone analogues materials have all been investigated as potential ZIB cathodes. Vanadium oxides are emerging as the most researched cathode material due to their high theoretical capacities (often $>300 \text{ mAh g}^{-1}$), low costs and stable layered structure [11].

1.2.1 Cathode Materials for ZIB

To achieve sustainable growth in employing renewable energy, innovative aqueous ZIB energy storage systems with vanadium oxide cathode material are seen as the best alternatives. Aqueous ZIBs consist of zinc metallic anode, separator, aqueous electrolyte and a suitable cathode material. The cathode of ZIB plays a crucial role in enhancing the storage performance through efficient insertion and subsequent extraction of zinc ions. Different materials are used as a cathode for ZIBs including MnO_2 , Prussian blue analogue, vanadium-based and organic compounds [7]. The performance of different materials is shown in Figure 2.

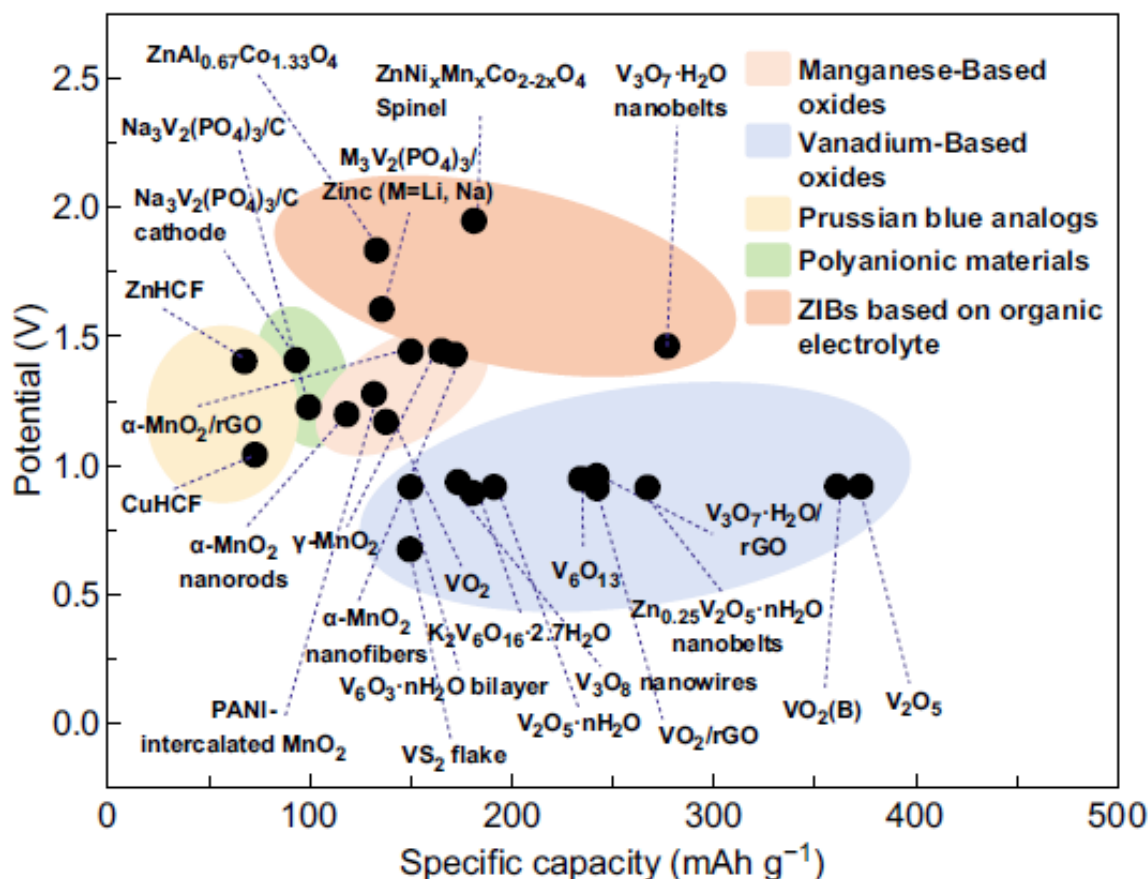


Figure 2: Comparison for specific capacities for different materials and oxides [12].

MnO₂ has high energy storage capacity but shows poor rate capability and poor cyclic stability while encountering an aqueous solution. Similarly, organic compounds and Prussian blue analogues exhibit a rapid decrease in storage capacity. Vanadium-based compounds have significant advantages due to high storage capacity, high stability, and open framework [13].

Fabricating cathode materials that are suitable for ZIBs with higher cyclic stability, and to achieve a wide range of operating voltage, and higher reversible capacities is still a challenging task. Divalent Zn²⁺ ions exhibit significant steric hindrance and stronger electrostatic attraction forces with the hosting structures, resulting in poorer cycle stability and slow kinetic intercalation rates [14]. Thus, compared to monovalent ionic batteries, the design guidelines of ZIBs for cathodic structures and materials are substantially different. Many different materials including organic compounds have been employed for cathode materials in ZIBs; however, these cathode materials have common problems such as dissolution of cathode, decrease in electrochemical efficiency, and collapse of material structure during cyclic loading. In fact, the functionality of cathode material is closely associated with their microstructures. Therefore, it is essential to have better understanding for the relationship between microstructures and energy storage performance to increase the overall efficiency of ZIBs. Research studies are focusing on different materials for energy storage devices [12]. Figure 3 shows different strategies that are employed to improve the performance of cathode materials in ZIBs.

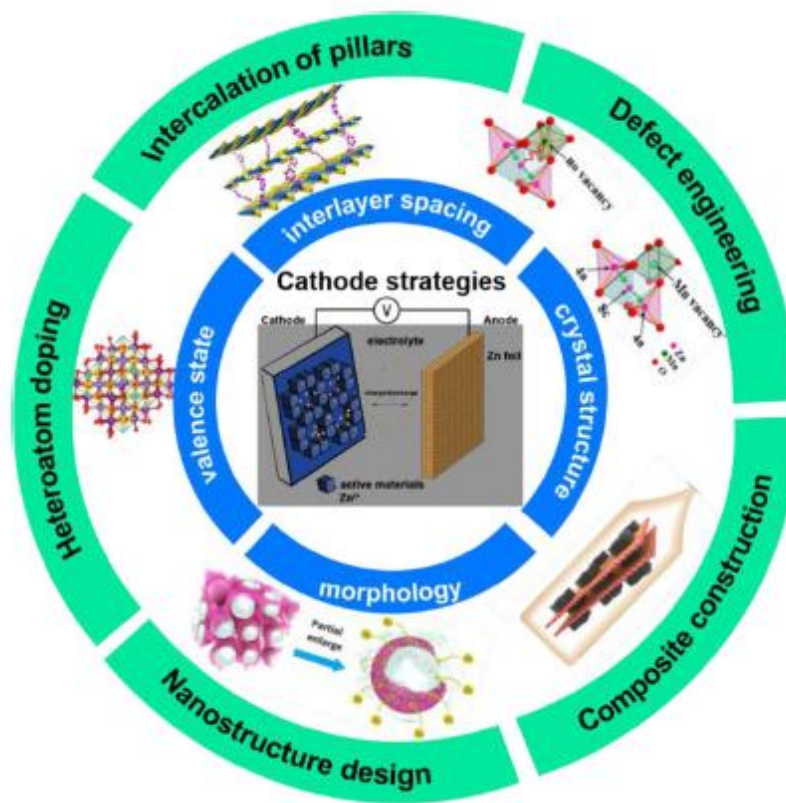


Figure 3: Different strategies to improve the performance of cathode materials in ZIBs [15].

Figure 4 shows ZIB structure along with the potential candidates for cathode materials. Figure 5 represents the interest of different research studies for different energy storage cathode materials in ZIBs. After Mn, vanadium is the most sought-after material for research studies. Considerable research studies are focusing on vanadium based compounds for cathode materials [16].

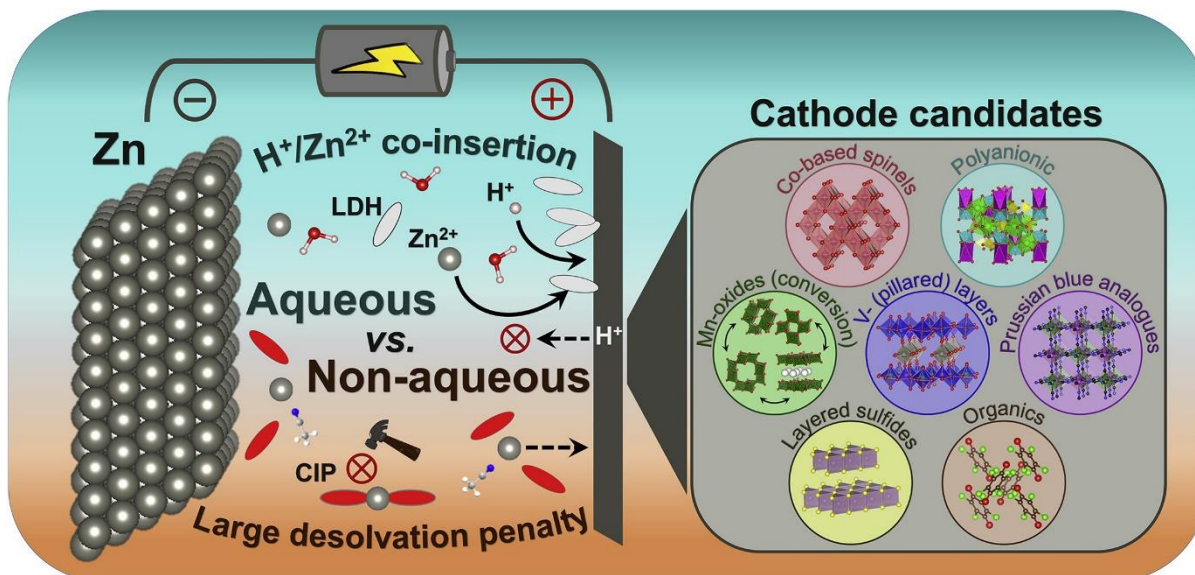


Figure 4: ZIB structure along with the potential candidates for cathode materials [17].

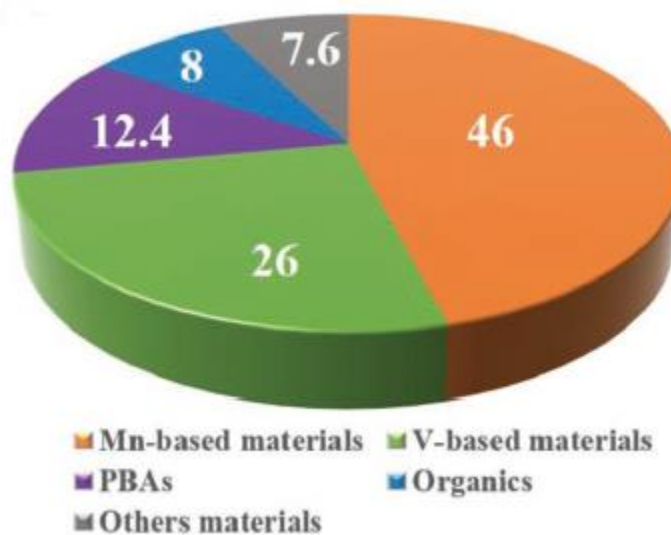


Figure 5: Pie-chart representing the ratio of publication of different energy storage materials [8].

1.2.2 Charge Storage Mechanism in ZIBs

Early ZIBs dates to the 19th century and used Zn and MnO_2 for disposable batteries. These batteries were not rechargeable that contributed to the waste generation and disposal problems. As the research and development progressed for these batteries, various other problems came to light

including dendrite formation, low performance efficiency and formation of undesirable by-products that further hampered the progress of ZIBs. The general storage mechanism for ZIB is shown in Figure 6.

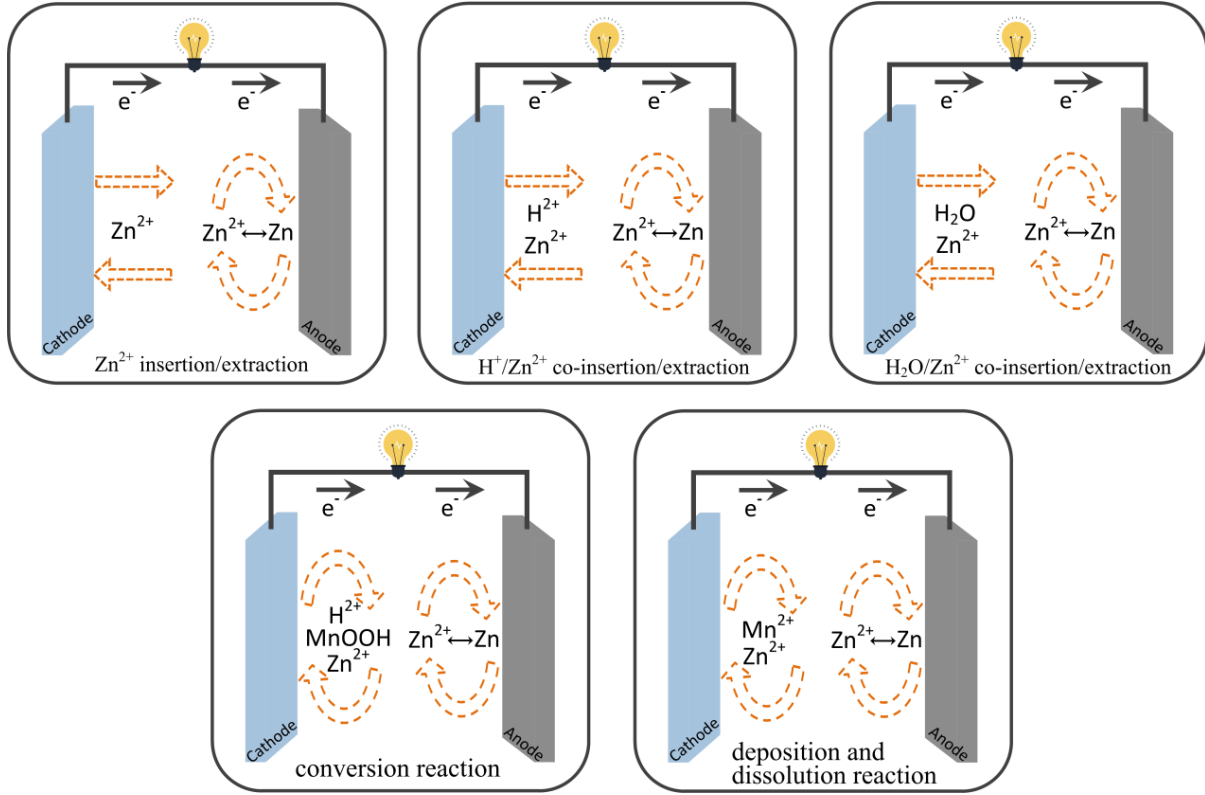
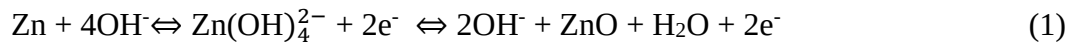


Figure 6: General Energy storage mechanism for Zn-ion battery [12].

To understand the root causes of these issues, it is essential to understand the working and charge storage mechanism of ZIBs. The charge storage mechanism in early alkaline based zinc batteries includes the chemical conversion of cathode materials that involved precipitation or dissolution reactions at Zn anode. The reaction is shown in equation 1 below [12].



The absence of intercalation and deintercalation reaction is clear and hence this cannot be named ZIB. Main components for ZIBs are Zn metallic anode, separator, aqueous electrolyte, and a cathode material that can accommodate to host Zn^{2+} ions. The charge storage mechanisms for typical ZIB are shown in figure 6. These mechanisms include Zn^{2+} ion insertion, dual-ion co-insertion, conversion reaction and co-ordination reaction. Anode material in ZIBs plays a simple role to provide reversible conversion of Zn/Zn^{2+} , therefore, the efficiency and performance of ZIB is dependent on the cathode materials and techniques employed to enhance the performance of the cathode material as explained earlier in figure 3 [18]. Cathode material in ZIBs acts as a charge carrier host for Zn ions and uses various electrochemical mechanisms for energy storage. Different cathode materials that are used in ZIBs are manganese oxides, vanadium oxides, Prussian blue analogues, crystalline structures along with other composite and polymeric materials. Each cathode material differs in reaction kinetics, operating voltages, cyclic stabilities, rate capabilities, and charging capacities.

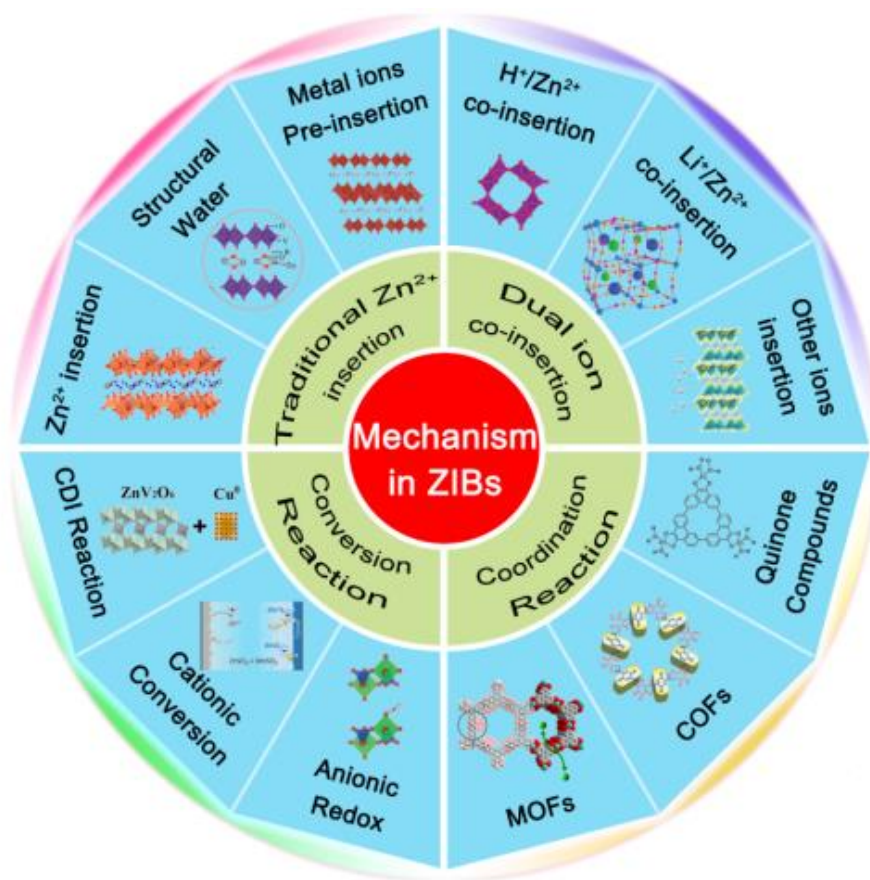


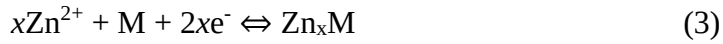
Figure 7: Different charge storage mechanisms for ZIBs [19].

Different research studies have tried to explain the charge storage mechanism for ZIBs but still, there are lot of ambiguities and mechanisms to understand. In addition to typical intercalation of Zn ions, there are other mechanisms that need to be understood to have sound knowledge to further improve the performance of ZIBs as shown in figure 7 [19]. The most common energy storage mechanism in ZIBs is insertion of Zn ions in the host material. The same mechanism is used in Li-based batteries for energy storage [20]. While discharging involves the intercalation of Zn ion in cathode material whose oxidation state is decreased by receiving electron. During charging, the cathode of ZIB releases Zn^{2+} ion. The whole charging and discharging process of ZIB is summarized in equations (2), (3) and (4).

Anode:



Cathode:



Overall Reaction:



M in these equations represents the cathode material of ZIB. Cathode materials that have layered, tunnel or open framework are the best candidates for cathode materials.

Chapter 2: Literature Review

Vanadium can be found in different valances (+5, +4, +3) and hence, different vanadium oxides, including layered and tunnel structures such as VO, VO₂, V₂O₅, V₂O₃, H₂V₃O₇, Zn_{0.25}V₂O₅ are used in rechargeable aqueous ZIBs [21]. The most notable of all these phases, VO₂ and V₂O₅, have been widely studied due to their extraordinary properties. The highest valence state of vanadium oxide is vanadium pentoxide (V₂O₅), which is also referred to as the most stable of all phases. This phase can exhibit electrochromic and thermochromic activity in certain situations. These factors contribute to the wide range of potential applications for Vanadium pentoxide. The applications range from catalysts to battery cathode, and gas sensors. Several techniques and methods can be used to fabricate V₂O₅ thin films. The surface and interfacial properties significantly affect the properties of thin films. As explained by M.B.Sahana et al. [22], the electrochemical properties of V₂O₅ films may differ significantly based on the fabrication process. The variation in properties is attributed to the thickness of films, fabrication methods, and materials. Vanadium oxide thin films can be fabricated using techniques including RF magnetron sputtering [23], vacuum-based evaporation [24], pulsed laser deposition [25], thermal oxidation [26], sol-gel [27], chemical vapour deposition [28], and pulsed dc based reactive sputtering [29]. Surface properties and material structures are more crucial for various applications and these properties are impacted by the fabrication processes and use of different substrate materials. VO_x films may be fabricated and altered following the intended function by selecting optimal fabrication parameters and post-production techniques.

Due to the open nature of the framework crystal structure and the existence of numerous oxidation states for vanadium, several vanadium-based cathode materials are being developed for aqueous zinc-ion batteries (ZIBs). In ZIB, vanadium is reduced and Zn²⁺ ion is inserted concurrently during discharging cycle as shown in figure 8.

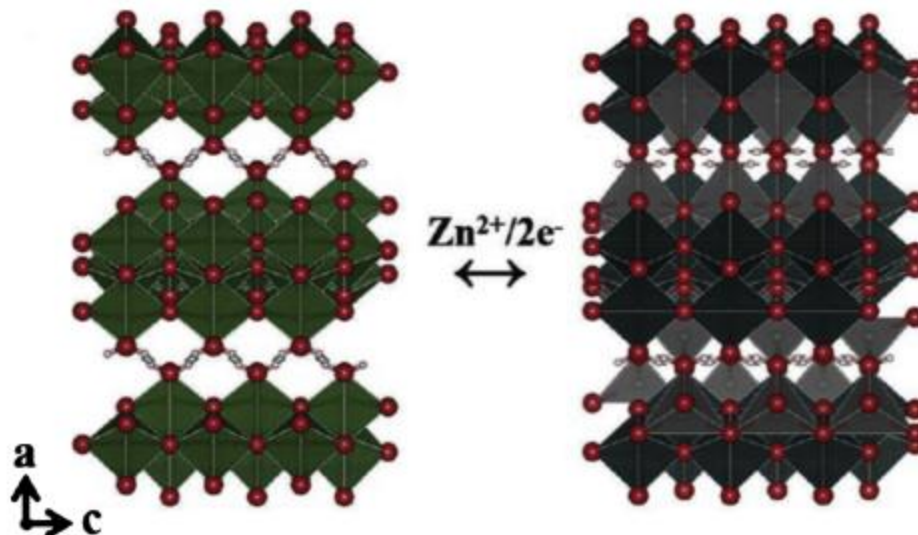


Figure 8: Zn²⁺ ion intercalation and de-intercalation process [30].

Zn has a large volumetric storage capacity of around 5,851 mAh/ml. Many alternative materials such as Al, Mg and Ca have comparable volumetric storage capacities but show poor electrochemical behaviour in the presence of an aqueous electrolyte. Vanadium compounds are active redox cathode materials that may be oxidized in the presence of oxygen to the lower valence state [31]. As a result, the oxygen in the surrounding atmosphere would oxidize the discharged vanadium cathode materials, just like the charging cycle. Due to these material advantages and developments, more efficient rechargeable ZIBs can be made with enhanced storage capabilities [32].

As shown in figure 10, solid solution or two single-phase domains corresponding to Zn_{0.55}V₂O₅ were separated by transition of a two-phase transition as Zn-intercalation progressed. Moreover, the width of interlayer could undergo contraction or expansion according to composition of thin layer of zinc during the Zn-intercalation and de-intercalation processes that are related to the ejection and absorption of electron from structural water at electrode [33]. Figure 9 shows graphical representation of intercalation/de-intercalation process for Zn ion during charging and discharging process.

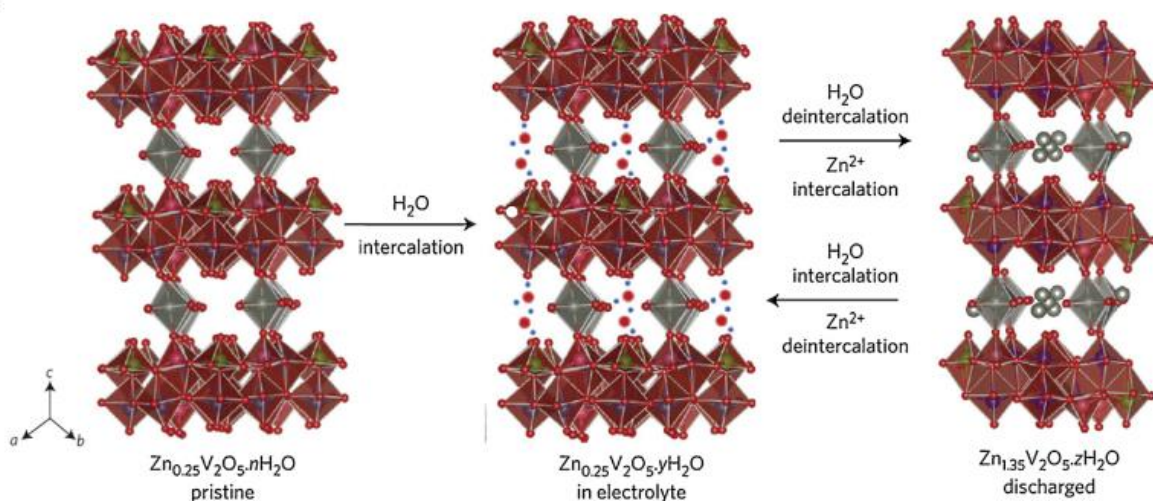


Figure 9: Graphical representation of intercalation/de-intercalation process for Zn ion during charging and discharging process [3].

Boruah et al.[34] achieved the conversion efficiency of 1.2% using ZIBs. The increased capacity of 140 mAh/g and retention of 83% capacity even after more than 500 charging/discharging cycles made ZIBs more reliable than Li-ion batteries. Zn metallic anodes were used for ZIBs. Zn anode performed significantly better than the Li-ion anode primarily due to enhanced stability and additional safety. Moreover, ZIB used cathode material based on a mixture of reduced graphene oxide (rGO) and vanadium dioxide (VO_2). The capacity for these electrodes reached as high as 282 mAh/g. It is concluded that vanadium-based compounds have a high charge retention ability of above 90% even after going through more than 1000 charging/discharging cycles. Cheng et al. [35] analyzed the energy storage of ZIB using a V_2O_5 cathode and aqueous electrolyte. Zn^{2+} ions can be extracted and inserted through the layered structure of V_2O_5 . Moreover, the charging and discharging process exfoliated nanosheets of V_2O_5 that contributed to achieving a high capacity of 372 mAh/g for energy storage. The high energy capacity was observed for more than 4000 charging/discharging cycles with a current density of 5 A/g. It was found that aqueous electrolytes significantly enhanced the transportation of Zn^{+2} ions. Charging and discharging mechanisms for of $\text{Zn}/\text{Zn}_{0.25}\text{V}_2\text{O}_5$ cell is shown in figure 10.

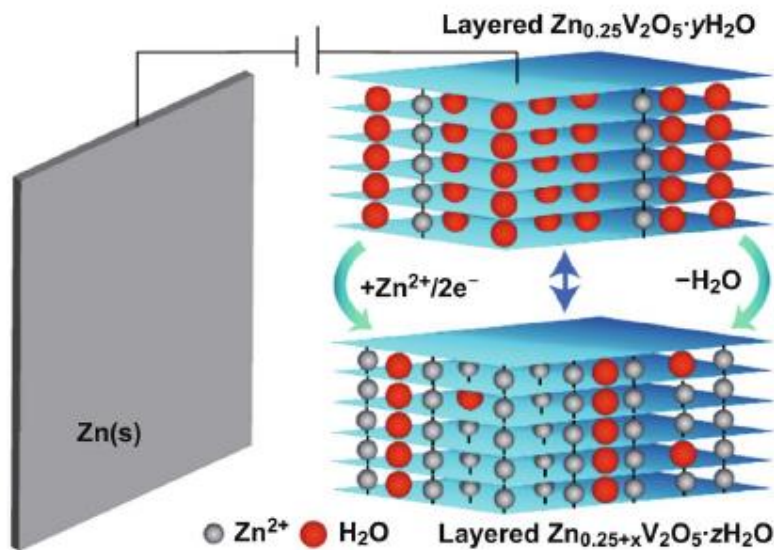


Figure 10: Graphical representation of Zn/Zn_{0.25}V₂O₅ cell [3].

Table 2: Electrochemical performance of different vanadium-based oxide materials for ZIBs. The table shows different parameters such as electrolytes, current, operating voltage, capacity retention, and capacity as analyzed in different research studies.

Cathode material	Electrolyte	Method	Current	Operating Voltage	Capacity Retention	Capacity	Ref.
VS ₂	ZnSO ₄ and aqueous solution	Electroplating	200 mA/g	Up to 1V	97% capacity retention after more than 250 cycles	125 mAh/g	[36]
VO ₂ and rGO	Aqueous	Combination of freeze-drying, high temperature reduction and mechanical compression	4 A/g	Up to 1.3V	99% capacity retention after more than 1000 cycles	240 mAh/g	[37]
V ₃ O ₇ ·H ₂ O and rGO	Aqueous ZnSO ₄	Electrochemical deposition method	1500 mA/g	Up to 1.5V	79% capacity retention after more than 1000 cycles	245 mAh/g	[38]

V ₆ O ₁₃	Zn(CF ₃ SO ₃) ₂ and Aqueous solution	Hydrothermal method	4 A/g	Up to 1.5V	92% capacity retention after more than 2000 cycles	240 mAh/g	[39]
V ₂ O ₅	LiTFSI + Zn(CF ₃ SO ₃) ₂ -			1.6 – 2 V	80% capacity retention after 2000 cycles	238 mAh/g	[40]
V ₂ O ₅	Zn(CF ₃ SO ₃) ₂	Electrospinning technique		0.5-1.5	81% of capacity retention after 500 cycles	156 mAh/g	[41]
VO ₂	ZnSO ₄	Hydrothermal method		0.2-1.3	86% capacity retention after 5000 cycles	325.6 mAh/g	[21]
H ₂ V ₃ O ₈	Zn(CF ₃ SO ₃) ₂	One Step hydrothermal method		0.2-1.6	94.3% capacity retention after 1000 cycles	423.8 mAh/g	[42]
H ₂ V ₃ O ₈ /graphene	Zn(CF ₃ SO ₃) ₂	Hydrothermal method		0.2-1.6	87% capacity retention after 2000 cycles	394 mAh/g	[43]
V ₃ O ₇ .H ₂ O	ZnSO ₄	Microwave solvothermal method		0.4-1.1	80% capacity retention after 200 cycles	375 mAh/g	[44]
V ₁₀ O ₂₄ . 12H ₂ O	Zn(CF ₃ SO ₃) ₂	Facile hydrothermal reaction		0.7-1.7	80.1% capacity retention after 3000 cycles	165 mAh/g	[45]
VS ₂	ZnSO ₄	Hydrothermal method		0.4-1	98 % capacity retention after 200 cycles	190 mAh/g	[46]

Vanadium and manganese oxides are the best tunnel structures such as α -MnO₂ with 2x2 tunnel structure, todorokite based MnO₂ with 3x3 tunnel structure, VO₂ with 3x3 tunnel structure [47]. Wang et al. [48] used VO₂ tunnel structure to achieve ultrafast charge storage in Li-ion batteries as shown in Figure 11.

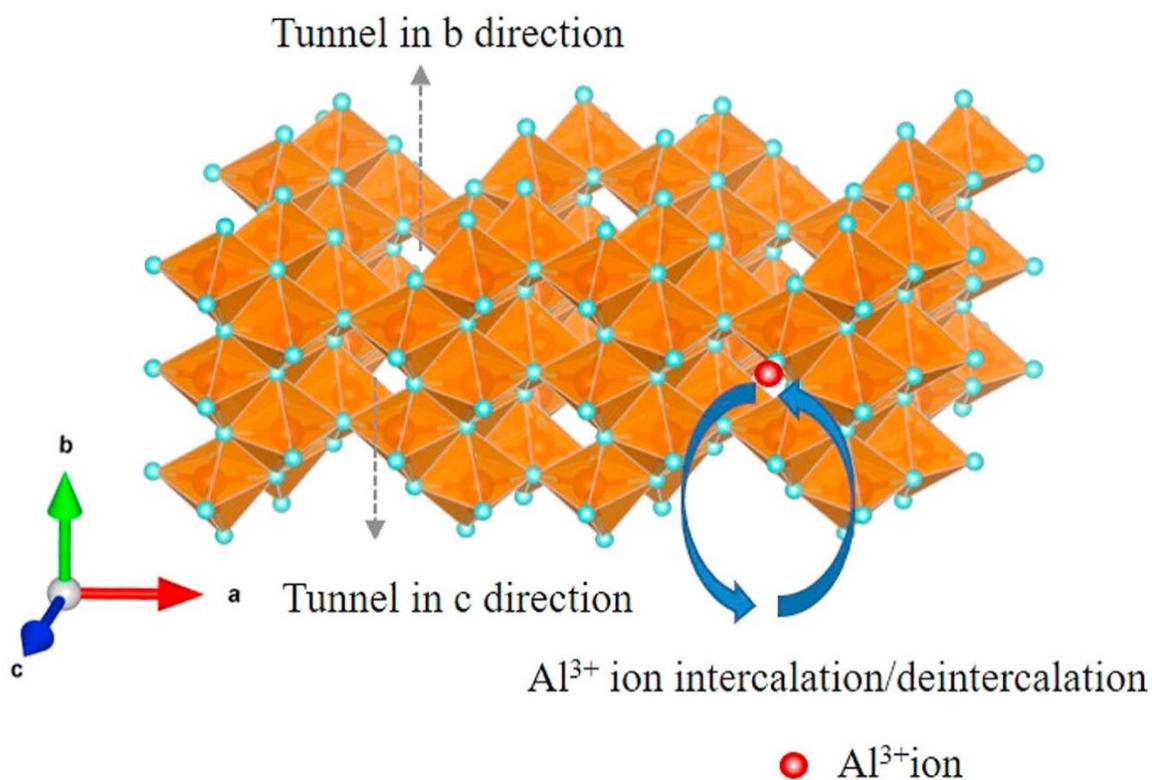


Figure 11: Intercalation and deintercalation of Al ion in tunnel structure of VO_2 [48].

Mn based tunnel structures have certain limitations such as degradation and phase change of cathode during electrochemical reactions while VO_2 tunnel structure possesses higher stability during these processes. Ding et al. [47] reported the use of VO_2 tunnels for highly efficient ZIB. Big size tunnels of 0.82 nm^2 along b-axes and 0.5 nm^2 along c-axes gave unhindered and smooth pathway for intercalation and deintercalation to Zn ion diffusion. VO_2 showed high power and energy density, rate capacity of 171 mAh/g and reversible capacity of 357 mAh/g . Figure 12 shows the unit cell expansion of VO_2 in a, b and c directions while discharging and contracts back and reverse the process during charging [21].

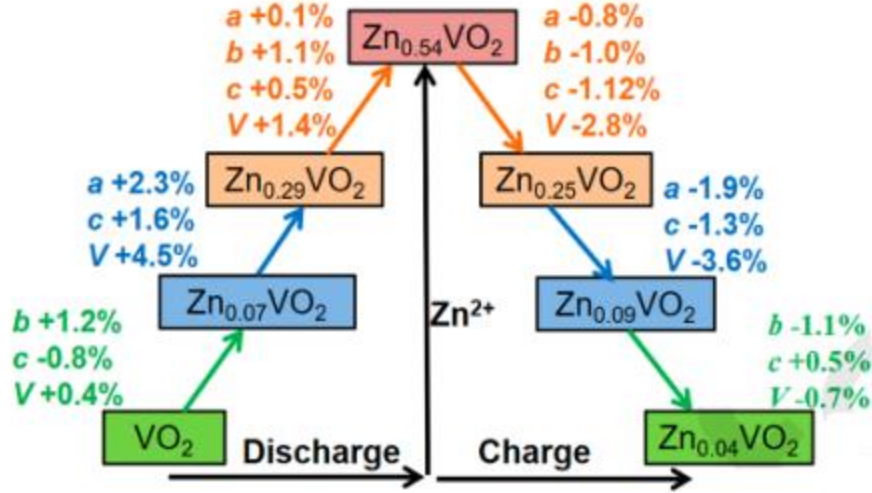


Figure 12: Tunnel single phase structure of VO_2 cathode during charging and discharging process [21].

2.1 Vanadium Oxide Cathode Thin Films

Vanadium oxide thin films are difficult to fabricate mostly due to the fact that vanadium exists in different stable oxidation states and several polymorphic forms. The properties of vanadium oxide thin films are dependent on morphology, film structure and stoichiometry. Different techniques are used to fabricate thin films of vanadium oxide including chemical vapor deposition (CVD), spray pyrolysis, atomic layer deposition (ALD), sputtering, electron beam evaporation, sol-gel, and liquid phase ALD. Most focused oxidation states for vanadium oxide are +4 and +5 due to the wide range of applications in semiconductor and energy storage applications. The formation of VO_2 thin film is a complex process and even the slightest change in process parameters can lead to the formation of variety of phases. Therefore, it is important to have complete control of fabrication process to achieve the desired properties [49].

Some of the challenges need to be addressed to make VO_x thin films with desired results such as preventing formation of higher oxidation states with the introduction of protective layer and control of process temperature to prevent undesired phases.

2.2 Challenges for Vanadium Oxide

ZIBs use aqueous electrolyte that can intercalate between layers of vanadium oxide cathode material. This electrolyte can effectively decrease the electrostatic forces of attraction between

layers of vanadium oxide and Zn ions resulting in reduction of charge that can in turn affect the performance of ZIB. The contact between cathode material and aqueous electrolyte lowers the diffusion barrier of Zn ions paving the path for swift migration that can in turn speed up the erosion or dissolution of vanadium oxide cathode. The dissolution of vanadium oxide cathode leads to the decrease in energy storage capacity and structural collapse. Multivalent metallic cations are known to support layered structure of V_xO_y by increasing the interlayer distance to prevent the dissolution [50]. Moreover, interaction of water with vanadium-based cathode can lead to poor charging/discharging. Minimizing the direct contact of water with vanadium oxide cathode material can significantly improve stability by preventing dissolution and cyclic stability. Most of the vanadium oxide cathode materials will eventually and slowly dissolve in aqueous electrolyte making it difficult for ZIBs in commercialization. Use of functional additives and solid electrolytes can prevent these issues of cathode degradation. Another way to solve this issue is the formation of cathode/electrolyte interfacial thin film to avoid direct contact, solid electrolyte interface is formed over cathode that prevents the degradation of cathode material. Guo et al. [51] analyzed the formation of solid electrolyte interfacial film over Ca_2MnO_4 cathode that contributed to reduce the contact of aqueous electrolyte in ZIB. The protective layer suppressed the dissolution of cathode materials and enhanced the cyclic performance.

Dendrite formation in ZIBs is one of the leading causes for the loss of efficiency and performance. Dendrite formation can lead to uncontrolled electrolyte consumption and severe loss in Coulombic efficiency [52]. The combined effect of dendrite formation in addition to dissolution of cathode and reaction with water limits the use of ZIBs. It is necessary to overcome these limitations to make ZIBs more efficient and highly stable. The main factor for dendrite formation is the solvation of Zn ion in aqueous electrolyte. Upon solvation, Zn ion forms $[Zn(H_2O)_6]^{2+}$ leading to a very high energy barrier for de-solvation and other water based side reactions and by products. The water molecules affect cathode materials through dissolution while it encourages the production of H_2 at anode [53]. H_2 production at anode can further lead to the formation passivation layer and change in pH of the local environment. Passivation layers such as ZnO and $Zn(OH)_2$ hinder the diffusion of electrons and ions that lead to the formation of dendrites. It is important to prevent these side reactions for high performance of ZIBs. The strategies to overcome these issues include the change and optimization of composition of the electrodes with the introduction of controlled passivation interface having enhanced ionic conductivity that can block electrons to hinder the formation of

dendrites [54]. Some of the limitations and issues of ZIBs with aqueous electrolyte are shown in Figure 13 [55].

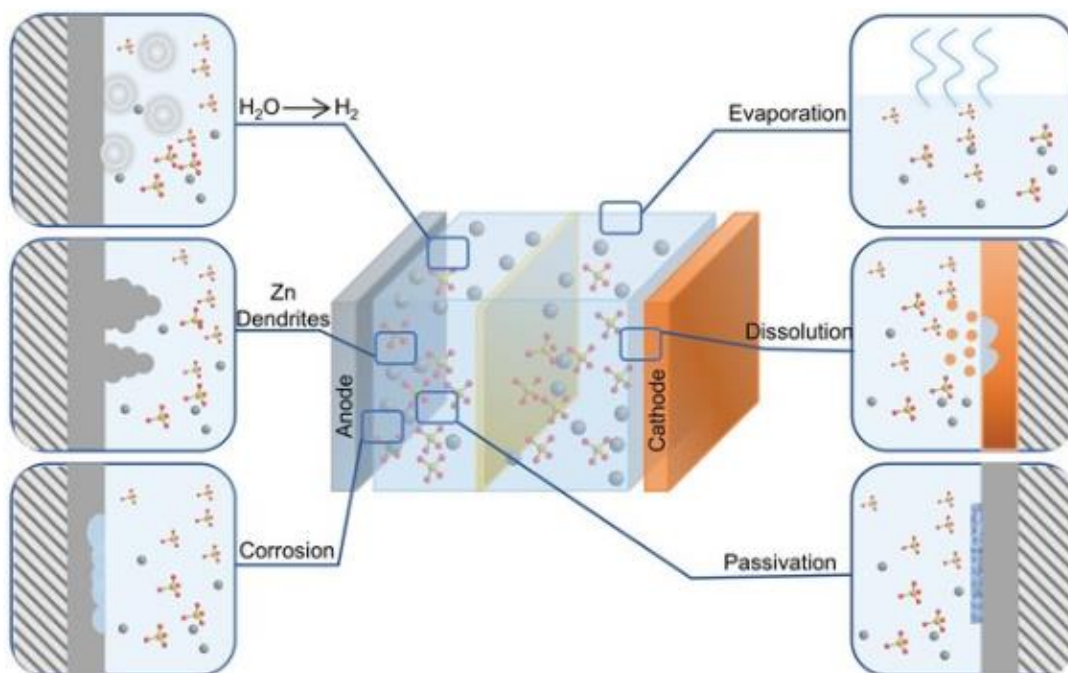


Figure 13: Issues and limitation of ZIBs with aqueous electrolyte [55].

Vanadium oxide is one of the most used cathode materials in zinc-ion batteries (ZIBs) due to high theoretical capacity, low cost, and eco-friendliness. However, certain challenges must be addressed before using vanadium oxide in ZIBs to increase the overall efficiency of the battery. One of the major challenges of using VO_x cathodes in ZIBs is their limited cycle life. Only after few hundred cycles, these cathodes start to experience a significant loss in capacity, leading to reduced cyclic performance and energy storage capacity [56]. Zinc ions start to deposit on the cathode surface during cycling, leading to the formation of passivation layer. The passivation layer further hinders zinc ion diffusion to affect the performance of the battery. Low-rate capacity is another issue with vanadium based cathodes and they exhibit poor kinetics for the intercalation/deintercalation of zinc ions, which can limit the overall power density and rate capability of ZIBs through low conductivity and slow kinetics [56].

Vanadium based cathodes have limited operating temperature range, leading to limited applications due to stability issues at higher temperature. Due to limited stability at high-temperatures, and the cathode will degrade rapidly above 400 °C. Moreover, at high temperature, vanadium-based cathode can become brittle making it difficult for these cathodes to perform in extreme temperatures. Scaling up the production of vanadium cathodes for use in ZIBs also pose challenges as the fabrication of pure vanadium cathodes requires precise control over fabrication process. The process needs to be scalable and cost-effective for commercialization of ZIBs [57].

Despite these challenges, research studies are focusing to develop strategies for these limitations and improve the performance of vanadium cathodes in ZIBs. Different approaches such as nanostructures, doping, and coating with thin films have been analyzed to improve the cyclic stability and energy storage capability of vanadium cathodes [49, 53-57]. New electrolytes and additives are being developed to prevent dendrite formation and enhance the safety of ZIBs.

2.3 Thin Film Sputtering

Sputtering is a widely used method for thin film deposition. The method includes the bombardment of source material or target ions. Ion bombardment and subsequent sputtering produce vapor phase. This process is physical that involves the formation of sputtered thin films from ion bombardment, therefore, the process is a part of physical vapor deposition techniques that include pulsed laser and thermal deposition. The most popular method to deposit sputtered material on a substrate is magnetron sputtering. In magnetron sputtering, the produced plasma discharge bombards the target [47]. Different methods are used to power the target such as Radio Frequency (RF) for non-conducting and Direct current (DC) for conducting targets, and several other methods to deliver voltage or current pulses to the target material [58]. Due to the physical nature of this process, the deposition of compound layers or thin films must be done with the addition of reactive gases to aid the process and uniform deposition. Reactive sputtering may have a non-linear flow of layer deposition due to high undesirable reactions of reactive gases. The quality, growth and properties of sputtered layer are dependent on flux and energy per particle of different species towards the target material [59].

DC sputtering is very popular to obtain non-reactive thin films. DC sputtering has advantages such as the production of thin compound layer films with controlled stoichiometry, control over film composition, high deposition rate suitable for industries, and high purity of films. Sputtering can

be used to deposit a wide range of elements, compounds, oxides, carbides, and alloys. The high economic cost of RF sputtering for non-conductive targets can be saved in the case of electrical conductive targets by using DC sputtering. Metal-based targets are ideal to achieve efficient cooling during sputtering due to which higher powers can be applied without compromising the quality of the thin film [60]. The basic schematic diagram for DC sputtering is shown in Figure 14.

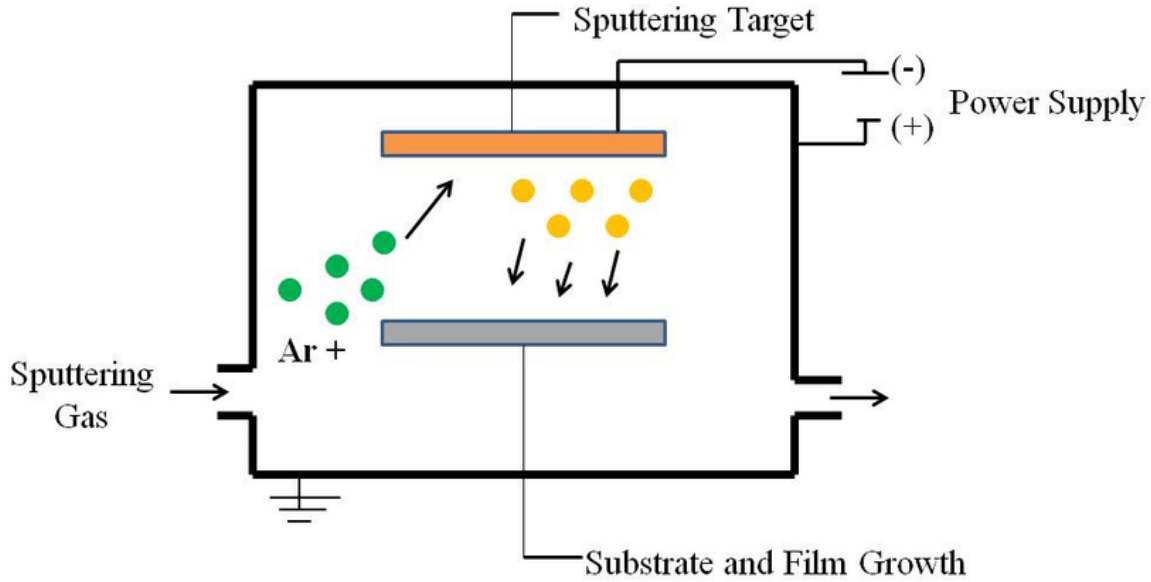


Figure 14: Schematic of DC Sputtering [61].

Sputtering seems to be a simple process but in fact, it is a fairly non-linear and complex process that is dependent on various independent factors. The presence of highly reactive flow gas not only reacts with sputtered ions but also causes target poisoning by reacting with the cathode surface. Cathode reactions are found to increase with the increase in the flow of reactive gas. The diversion of reactive gas for cathode reactions can affect the deposition rate and plasma of the sputtering system. Another issue with DC sputtering is arc formation which can severely limit the quality of the thin film and cause local melting. Even with all the limitations, DC sputtering is the most used sputtering technique [62].

Different methods are used to fabricate vanadium oxide thin films [65]. These techniques involve sol-gel method, electron beam evaporation, vapor deposition, pulsed laser ablation, resistive

heating and sputtering. Sputtering is one of the most commonly used processes to obtain high-quality thin films with good reproducibility. Most vanadium oxide thin films produced through sputtering use pure vanadium metal as the target material. Vanadium is a viable target material for sputtering and VO₂ deposition in combination with reactive gases such as argon and oxygen. Vanadium oxide have different oxidation states from II to V, therefore, it is critical to get to the right oxidation state for desired properties. Kang [63] explained the factor influencing the composition and oxidation states of vanadium oxide. These factors are deposition temperature and mole fraction between V and O. Inability to control sputtered vanadium and oxygen ratio in the reactive gas mixture makes it difficult to obtain optimal VO₂ deposition even with the knowledge of exact mole fraction from the literature. The fine-tuning of factors and variables including O₂/Ar ratio, substrate temperature, operating pressure and structure, is required to gain control over V and O mole fractions. The effects of the variables like substrate temperature and reactive gas ratio can be seen more clearly without any post-annealing. Yuce et al. [64] fabricated VO₂ thin film by optimizing and controlling the reactive oxygen gas flow ratio while maintaining a constant substrate temperature of 550 °C for one hour with operational pressure of 0.85 Pa and 50 W power. Details about the sample are shown in table 3.

Table 3: Sample details such as deposition time, oxygen ratio and thin film thickness [64].

Sample Name	Deposition Time (min)	Oxygen Ratio (%)	Thickness (nm)
A	45	2	310
B	22.5	2	120
C	22.5	2.25	125
D	22.5	2.50	124
E	22.5	3	127

As shown in Raman spectra in figure 15, there is a direct relationship between oxygen flow rates and the deposition of V₂O₅ thin film. A high ratio of oxygen in flow gas leads to a high mole fraction of oxygen, therefore, the formation of high oxidation vanadium oxide. Vanadium (V) formation was preferable to vanadium (IV). Electric and optical properties of deposited vanadium oxide thin film confirmed the presence of VO₂ at an oxygen level of 2.25%. For higher oxygen

levels, the results were not consistent with the available data. In conclusion, phase formation for vanadium oxide is dependent on the mole fraction and oxygen ratio in flow gas.

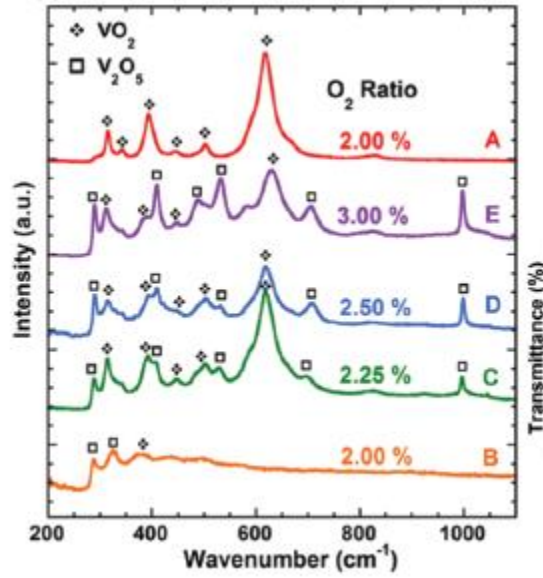


Figure 15: Raman Spectra of different vanadium oxide samples with variable oxygen ratio [64].

Zhao et al. [65] prepared seven different samples of vanadium oxide with a thickness of 120 nm. Different substrate temperatures ranging from 550 °C up to 700 °C were used along with constant pressure of 0.4 Pa and oxygen flow gas ratio of 11%. As shown in the SEM results in figure 16, the final thin film surfaces had large grains and rough surfaces.

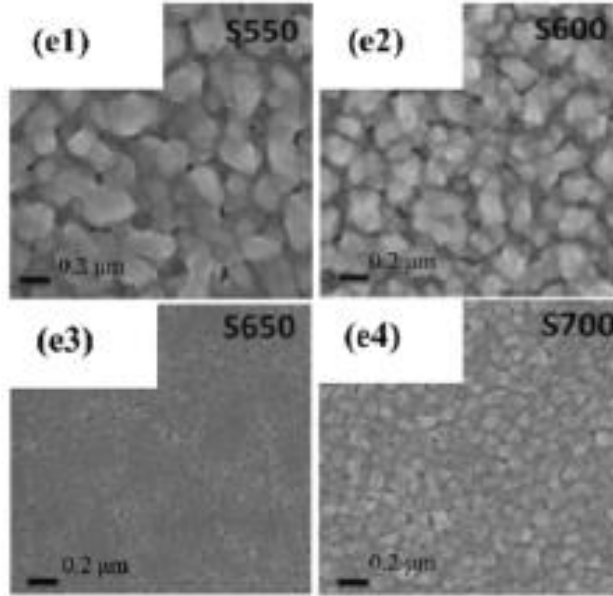


Figure 16: SEM images for vanadium oxide thin film surfaces [65].

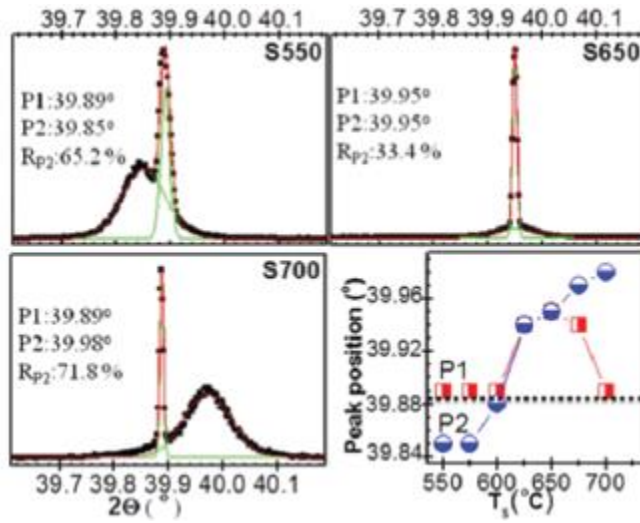


Figure 17: XRD spectra of vanadium oxide samples [65].

XRD spectra of vanadium oxide thin films are shown in figure 17. The double peak clearly shown in this spectra is due to the transition in VO_x from transition state V to IV and then to III after the increase in substrate temperature. Other phases during a transition such as V_2O_5 and VO_2

contributed to the formation of a double peak in XRD spectra. This research study briefly explained the role of substrate temperature on the stoichiometry of deposited vanadium oxide thin films [65].

Research studies have used two approaches to fabricate thin film of vanadium oxide. The first approach used DC sputtering along with high-temperature air annealing to deposit thin films. The properties of this vanadium oxide thin film are dependent on the annealing temperature. While the second approach uses reactive sputtering plasma with controlled addition of oxygen during the sputtering. Temperature during the reactive sputtering varies from 300 to 700 °C. The properties of the obtained thin film may be improved by post-process annealing.

2.4 Role of Annealing on Sputtering

Annealing after sputtering of metal oxide ensures the high quality of the thin film. Annealing makes sure the crystallization of amorphous film along with the purging of reactive flow gas to maintain the quality of the film. Yu et al. [66] fabricated VO₂ film at room temperature using 0.06 Pa of operational pressure, 90 W power and a variable ratio of oxygen flow gas. The low temperature of the substrate resulted in the formation of amorphous vanadium oxide thin film. Post annealing process at 400 °C ensured the transition to crystalline structure from the amorphous film. Sometimes, inert gas is added during annealing to maintain the stoichiometry of film composition. Post-annealing was found to increase the quality of vanadium oxide thin film significantly.

Dou et al. [67] used a 2-step annealing process to vanadium oxide thin films. Vanadium oxide thin films were deposited with 1 Pa operational pressure, 550 °C, and a reactive oxygen flow of 2%. Obtained vanadium oxide thin film was first annealed at 500 °C for crystallization for 400 seconds and pressure of 220 Pa. Thin film was further oxidized at atmospheric pressure and 450 °C for 200, 400, 600 and 1000 seconds. As shown in the XRD spectra in figure 18, a decrease in vanadium oxide was observed with the increase in oxidizing or annealing time. An increase in V₂O₅ was observed due to the transition of vanadium to state V.

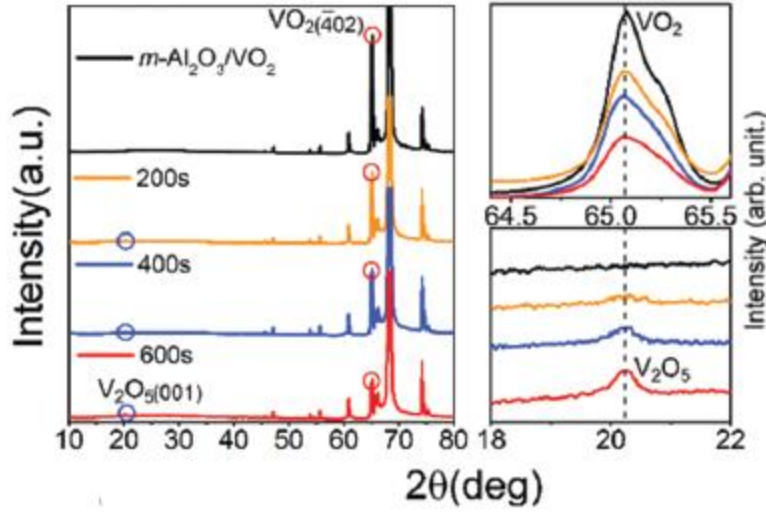


Figure 18: XRD spectra of annealed or oxidized vanadium oxide [67].

The effects of different substrate materials may not play as important role as the reactive flow gas ratio does. Xu et al. [68] analyzed the deposition of vanadium oxide at room temperature. 0.63 Pa operational pressure, 200W power, and reactive flow gas ratios from 25% to 50% were used. Sputtered and deposited film was later annealed at 450 °C for 120 min. XPS spectra of the vanadium oxide thin film in figure 19 showed that as the ratio of reactive gas was increased, the transition of vanadium oxide from III to V oxidation state accelerated.

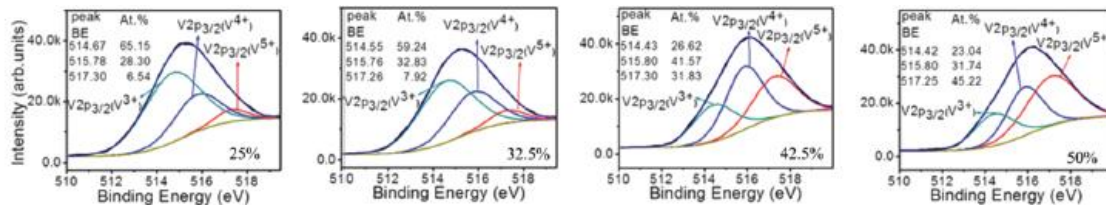


Figure 19: XPS spectra of vanadium oxide films [63].

It is concluded that post-annealing does not have as significant effect on the transition of VO₂ to V₂O₅ as the reactive flow gas ratio has. The post annealing process is seen as a powerful tool to correct the stoichiometric composition of a vanadium oxide film. Excessive annealing can have undesired effects and can affect the functionality of thin film.

This study uses a novel approach to fabricate vanadium oxide thin films as cathode materials for ZIBs. The study investigates the use of vanadium oxide as a highly efficient cathode material and compares two different approaches to create the thin films and analyzes the effects of annealing temperature and oxygen gas during sputtering. Moreover, the study utilizes different characterization technique, such as cyclic voltammetry, GCD, electrochemical impedance spectroscopy, and optical profilometry to thoroughly evaluate the performance of VO cathode materials. This multi-faceted approach provides a deeper understanding of electrochemical properties and performance of vanadium oxide thin films as cathode materials, for future R&D in energy storage devices. The study highlights the importance of new materials and fabrication techniques to enhance the efficiency of energy storage devices.

2.5 Objectives

The primary objective of this work is to make use of an easy one-step thin film deposition technique (DC magnetron sputtering) of Vanadium to apply it in ZIB cathode material development. The thickness of the film and the effect of the different oxidation temperature of the sputtered films were investigated.

This study aims to investigate thin film deposition for vanadium-based cathode materials for zinc ion batteries. The objectives are:

- Synthesis of thin film vanadium oxide materials by sputtering techniques for ZIBs.
- Characterization of the as-prepared materials using techniques such as XRD, SEM, and Optical Profilometer.
- Fabrication of ZIB coin cell.
- Comparison of different approaches for cathode fabrication.
- Evaluation of the performance of the ZIBs to check the sustainability of these devices.
- Performance investigation knowing deposition parameters for vanadium oxide.
- To provide alternatives to the issues in the performance of fabricated ZIBs

Chapter 3: Experimental Procedure

3.1 Fabrication of Coin cell

Coin cell has main components such as cathode, anode, and electrolyte. Oxidation occurs at the negative terminal of the coin cell during discharging. From there, the current flows into the external circuit. The cathode is responsible for reduction reactions that act as a positive terminal during discharging and electrons flow to the cathode after passing through the external circuit. Both anode and cathode materials must be stable at the electrolyte/electrode interface. Cathode material must have good reducing agent properties, high conductivity, ease in fabrication and be economical. Electrolyte plays an important role to determine the efficiency of the coin cell. The conductivity of the electrolyte must be between 10^{-5} and 10^{-2} S/cm as electrons are transported between electrodes through the electrolyte. The ionic transference number for electrolytes should be greater than 0.9 [69,70]. The general schematics for coin cells are shown in figure 20. The fabrication of coin cells needs instruments like pressure-controlled crimper and disc-cutting machines. These machines are shown in Figures 21 and 22.

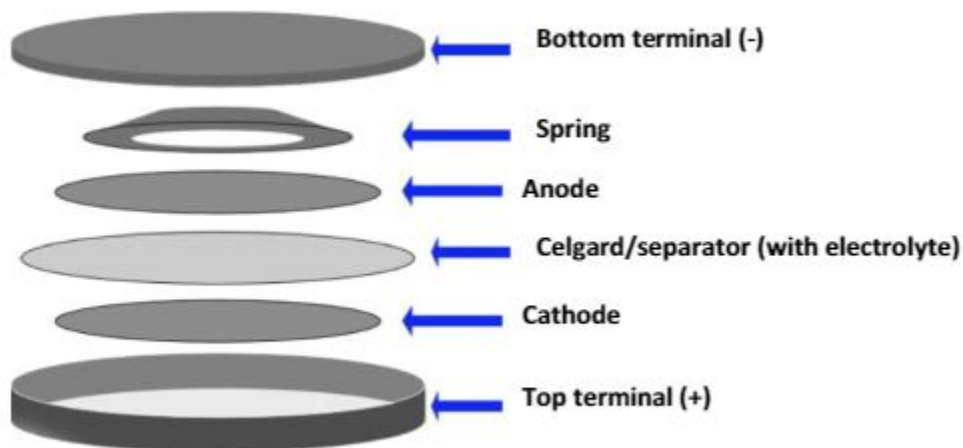


Figure 20: General schematics for fabrication of a coin cell battery.



Figure 21: Pressure controlled crimper used for coin cell fabrication.



Figure 22: Disc cutting machine for coin cell fabrication.

3.2 Material Synthesis

Cathode are prepared using a coin cell size cut of titanium foil with a thickness of 100 μm . Ti foil substrates are cleaned with Acetone, IPA and De-ionized water and then dried for 5 minutes on a hotplate at 100 $^{\circ}\text{C}$. After this, the samples are loaded inside a Nano-master NSC-4000 vacuum chamber. A base pressure of 1×10^{-4} torr is maintained before starting the deposition process. The target material is vanadium metal installed in a DC magnetron sputtering gun. The power is set to 100 W for 2-inch target. Several depositions result in 0.5 μm , 1 μm and 2 μm layer of vanadium on the Ti foil substrates. Normally, Argon pressure is set to 70 sccm during sputtering making the deposition pressure to be 4×10^{-3} torr. The setup for sputtering is shown in Figure 23.



Figure 23: Sputtering setup for the fabrication of VO cathode material.

The formation of vanadium oxide thin films is done by two methods: annealing metal sputtered samples in a tube furnace in air environment at different temperatures and sputtering with oxygen gas. The annealing time is set to 120 minutes with a ramp rate of 5 $^{\circ}\text{C}$ per minute both in heating and cooling. The other method is by equalizing the Argon pressure inside the chamber to oxygen introduced while sputtering (35 sccm Ar: 35 sccm O_2).

3.3 Material Characterization Techniques

XRD data has been recorded through Rigaku Miniflex-II at constant scanning rate of 2 degrees per min. by X-ray diffractometer with Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$). For image processing, the scanning electron microscopy (SEM, JEOL) has been used to check surface morphology and properties of thin films. The Profilm3D optical profiler is used to determine the thickness of the deposited films which uses state-of-the-art white light interferometry (WLI) to measure surface profiles and roughness down to $0.05 \mu\text{m}$.

3.4 Electrochemical Characterization techniques

The as prepared cathode has been used for electrochemical analysis, the working electrode was cut into small pieces with specific diameter (15 mm). After that, the cathodes were tied up with Zinc foil, electrolytes, suitable separator and finally assembled into ZIB coin cells of varying thicknesses are tested a Landt Battery tester for charge and discharge test with a current density of 100 mA/g and a voltage window of 0.2V to 1.8V. Additionally, the galvanostatic charge/discharge (GCD) curves, cycle performances as well as rate performances were carried out on Chi440c test system at different current densities. Cyclic voltammetry was carried out on the CHI760e instrument at different scan rates at a fixed voltage range. The Electrochemical Impedance spectroscopy (EIS) is performed at frequency range 0.001 to 100,000 Hz. The flow chart of this study is shown in Figure 24.

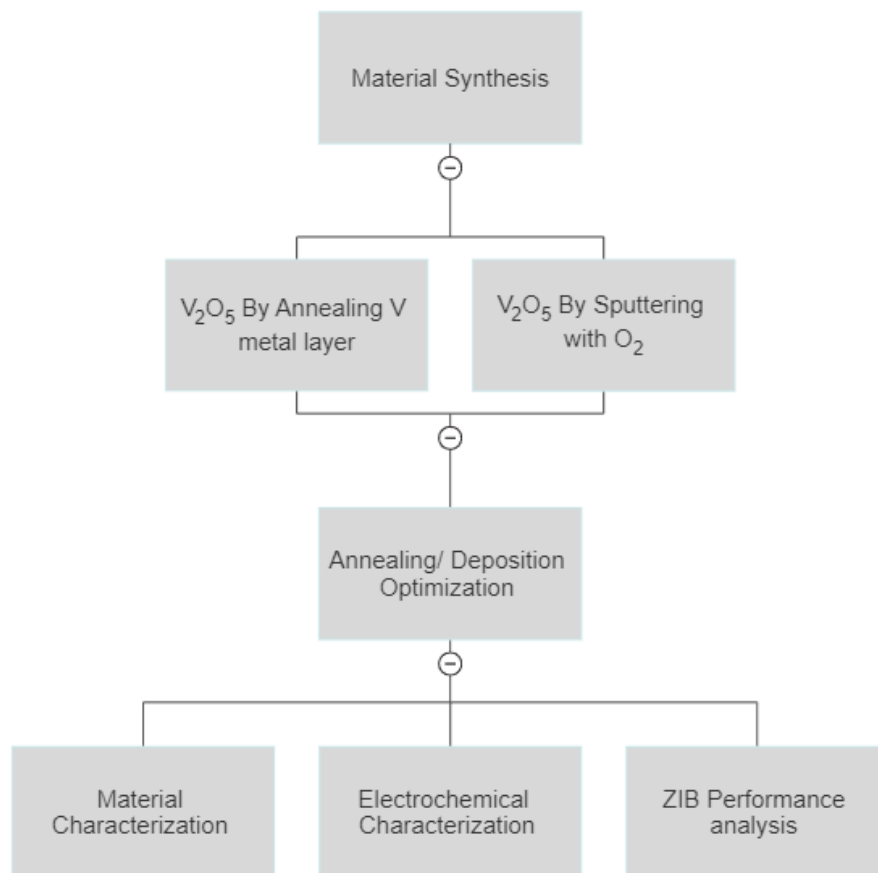


Figure 24: Flow-chart of this research study

Chapter 4: Results and Discussion

4.1 Crystallographic and Microstructural Analysis

In this section, it is aimed to develop one-step sputtered thin film vanadium oxide cathode for Zinc Ion Batteries (ZIBs). Two approaches are used to fabricate thin film vanadium oxide thin films. The first approach uses sputtered vanadium metallic layer using DC sputtering technique and oxide layer is formed by annealing the metallic layer at different temperatures. The effect of variation in annealing temperature is used to analyze the difference in properties and performance of vanadium oxide thin film as a cathode in ZIBs. The second approach uses the addition of oxygen gas during sputtering of vanadium metal for oxidation to get final vanadium oxide layer.

4.1.1 X-Ray Diffraction (XRD)

The two-dimensional (2D) layered vanadium oxide nanostructure is grown on coin cell-size titanium foil of varying thickness via DC magnetron sputtering. This sputtering method gives a unique material morphology and structure due to the direct interaction of the active materials on the conductive substrate without use of any binder.

Figure 25 shows XRD pattern for synthesized crystalline material V_2O_5 on titanium foil with thickness of 0.5 μm and 1 μm at 600 °C post-annealing temperatures. The XRD reveals the presence of main diffraction peaks for monolithic and crystalline vanadium oxide demonstrating the successful formation of oxidized layer. Moreover, the transition of monolithic vanadium to bilayer structure is observed that has the ability to adjust the diffusion of Zn ions during cycling due to variation in volume of the thin film structure.

XRD patterns of post-annealed Vanadium Oxide thin films is shown in Figure 26 at different post-annealing temperatures. The XRD patterns reveal the successful formation of crystalline V_2O_5 phase along with monoclinic structure, which is consistent and in accordance with the literature. (PDF in Match Software:96-412-4512). The identified diffraction peaks corresponding to the (200), (001), (101), (110), (301), (011), (020) and (012) planes for V_2O_5 crystal structure are clearly observed. The 2θ angles for each are as follows: 16°, 21°, 22°, 28°, 33°, 34°, 51° and 54°. The intensity of peak for (001) plane increases as the annealing temperature increases as shown in Figure 27, that is the indicator for the improvement of crystallinity in V_2O_5 phase. This also reveals

that higher annealing temperature promotes the growth of larger V_2O_5 crystallites and contributes to improving the crystallographic alignment in the thin film. But high annealing temperatures and annealing time can lead to the formation of some unwanted phases and regions, that can significantly affect the performance of the cathode material in ZIBs.

Figure 26 shows XRD pattern for V_2O_5 thin film fabricated by annealing of sputtered vanadium oxide film at 200, 400 and 600 °C. The XRD pattern confirms the formation of V_2O_5 crystalline phase and the presence of monoclinic crystal structure. The peak intensity of (001) at 2θ angle 21° plane is much lower or non-existent for the film formed with oxygen gas in comparison with thin films formed by annealing as shown in Figure 27. This suggests the lower degree of crystallinity (amorphous nature) for the thin film formed in the presence of oxygen [71,72].

Overall, the first approach exhibits the formation of crystalline V_2O_5 with higher crystallinity likely due to large crystallite growth of V_2O_5 particles and better crystallographic alignment. Second approach exhibits formation of amorphous material structure. The results are consistent with the literature [71,72].

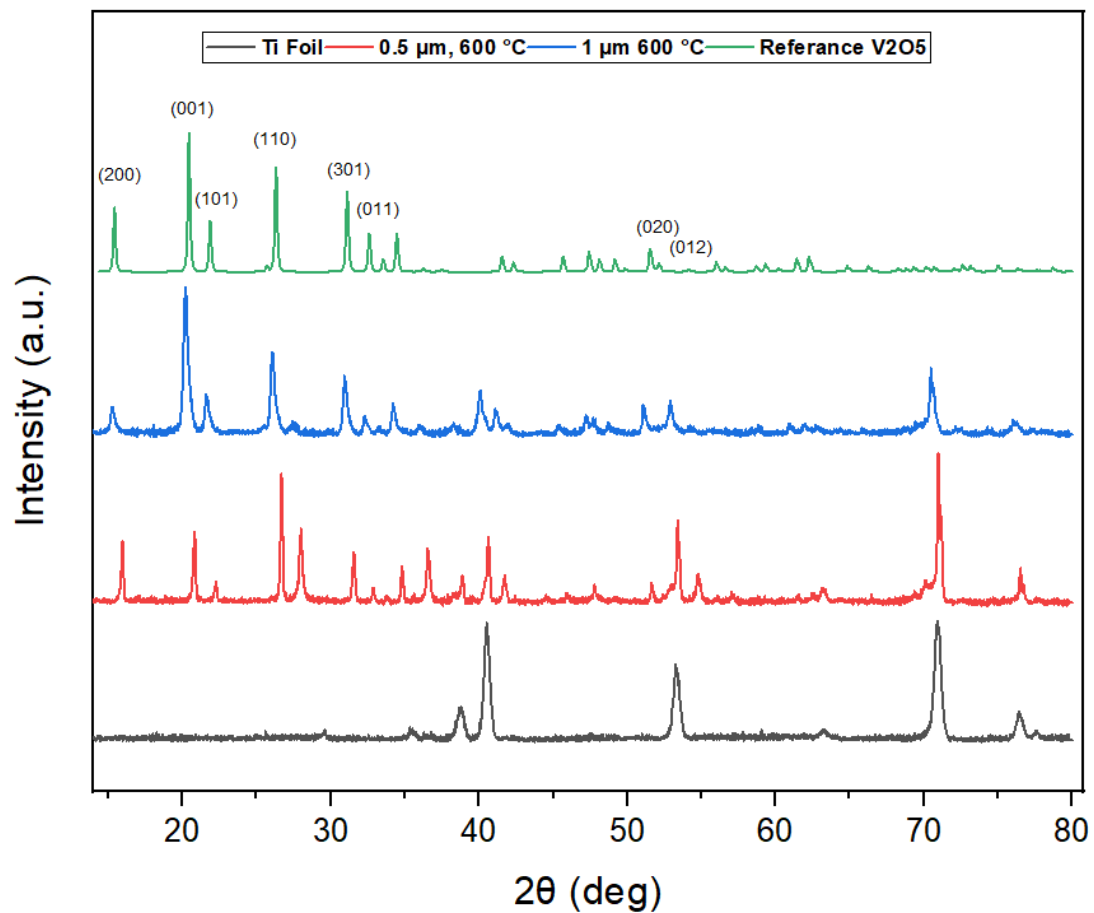


Figure 25: XRD pattern of Ti foil substrate, reference V₂O₅, 0.5 micron and 1 micron Vanadium Oxide prepared by post-annealing treatment of sputtered V thin films at 600 °C

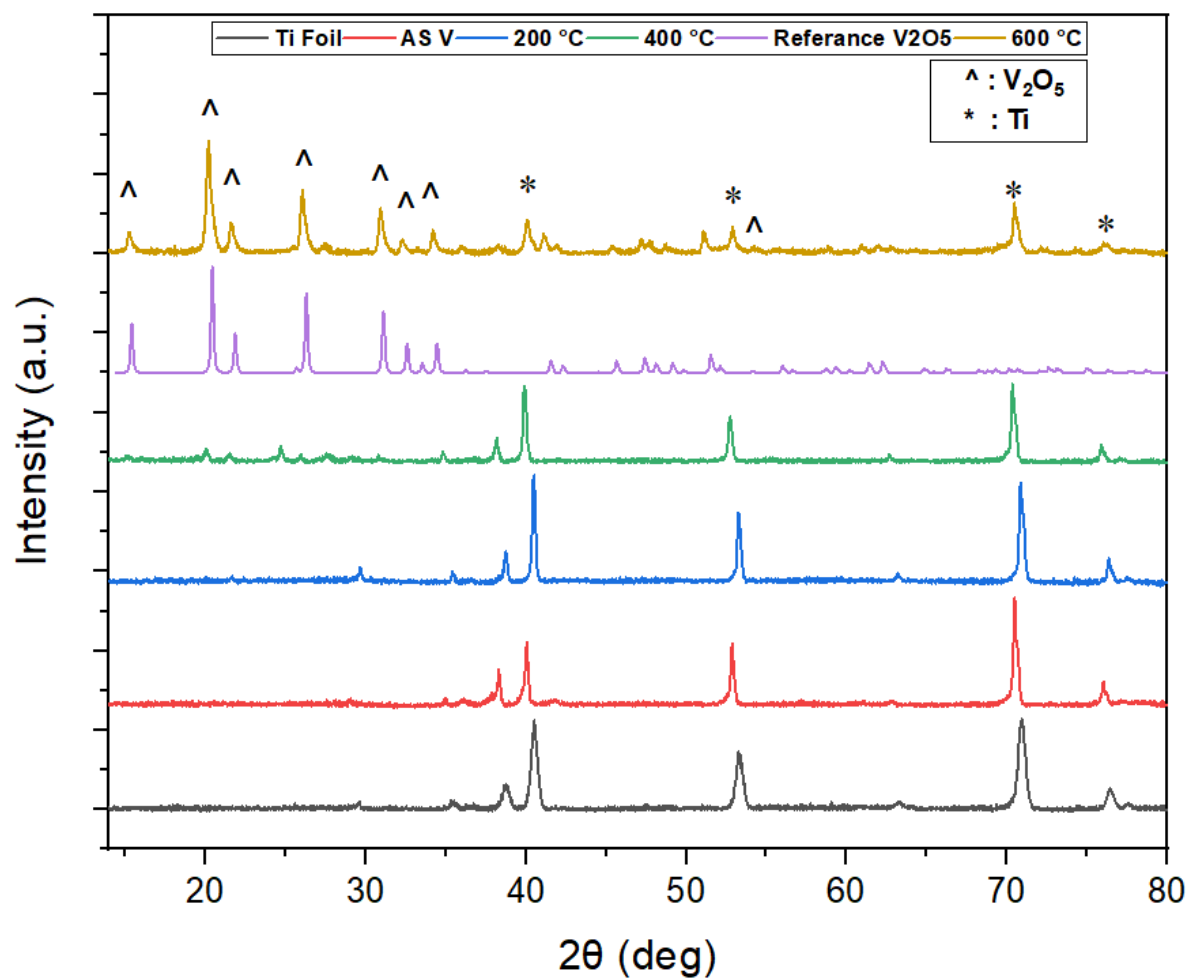
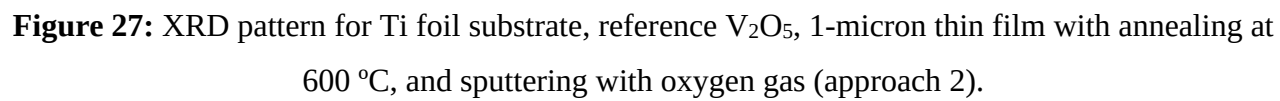


Figure 26: XRD pattern for Ti foil substrate, reference V₂O₅, Vanadium oxide prepared by post-annealing treatment of sputtered V thin films at 200 °C, 400 °C and 600 °C.



4.1.2 Scanning Electron Microscope (SEM)

The analysis of Scanning Electron Microscope (SEM) analysis showed the formation of Vanadium and oxide thin films for both the approaches but both approaches have different morphologies and structures.

Using the first approach, where the vanadium metal thin film was sputtered using DC sputtering and then oxidized by post-annealing in air, the SEM images show that with the increase in annealing temperature, the oxide film surface becomes rough with a more uniform microstructure as shown in Figures 28 and 29. This is due to the change in surface roughness and growth of oxide particles due to variation in annealing temperature. The formation of such structure in the oxide layer benefits and improves the electrochemical performance when used as cathode in ZIBs. The formation of uniform Vanadium oxide micro-flakes on Ti foil substrate can be observed for 1 μm and 2 μm thickness of oxide layer at different annealing temperature starting of 400 to 600 $^{\circ}\text{C}$. The interlining spaces observed for annealed vanadium oxide layers are used for intercalation and deintercalation of Zn ions during charging and discharging. The particles of Vanadium oxide grew along the substrate and flake like structure is formed after annealing. The growth of small flakes to large ones further increased the surface area of the oxide film. The diameter on Vanadium oxide particle ranges from 1 μm to 2 μm . These Vanadium oxide flakes are great conductors of electricity and are connected to each other making it easier in the formation of a highly conductive framework. The large surface area with open spaces can accommodate the movement of active material ions during cycling that can in turn enhance the performance of Vanadium oxide cathode material in ZIBs. The flake like structure presents a unique combination in structure with increased conductivity, active material sites, path for intercalation and deintercalation of electrolyte ions and high surface area. These structures are not only useful for applications of ZIBs but are also highly desirable for other applications such as solar cells, supercapacitors etc. Few defects such as pores and cracking can be observed specifically in Figure 28 possibly due to annealing effect on thicker films which can cause cracking and damage the oxide layer surface. Another possibility of such defects can be due to issues in bonding between Vanadium oxide and substrate material during sputtering. The slow growth rate in Figure 28 may also contribute to such undesired defects. It is also observed that pore size of defect is directly related to the thickness of the metal layer. The pore size is more uniform with metal layer thickness of 1 μm . Optimized annealing time and thickness can give far better results for the morphology of Vanadium oxide thin film.

The second approach with the introduction of oxygen gas along the sputtering process exhibits a very dense and smooth film. The Vanadium oxide layer contains very few defects and has larger grains in comparison with the first approach. The reason behind this is the formation of oxide layer during sputtering process due to introduction of oxygen gas leading to a more uniform oxide layer. The comparison between these two approaches reveals that the vanadium oxide layer formation with oxygen gas gives better results in terms of uniform morphology, particle size and structure as shown in Figure 31 but the benefits of flake like structure are more desirable. Introduction of oxygen gas saves the additional time required for annealing. The dense and uniform structure in the second approach can lead to higher efficiency and longer cyclic life but Vanadium oxide flake like structure are more desirable for battery applications as explained in first approach [31].

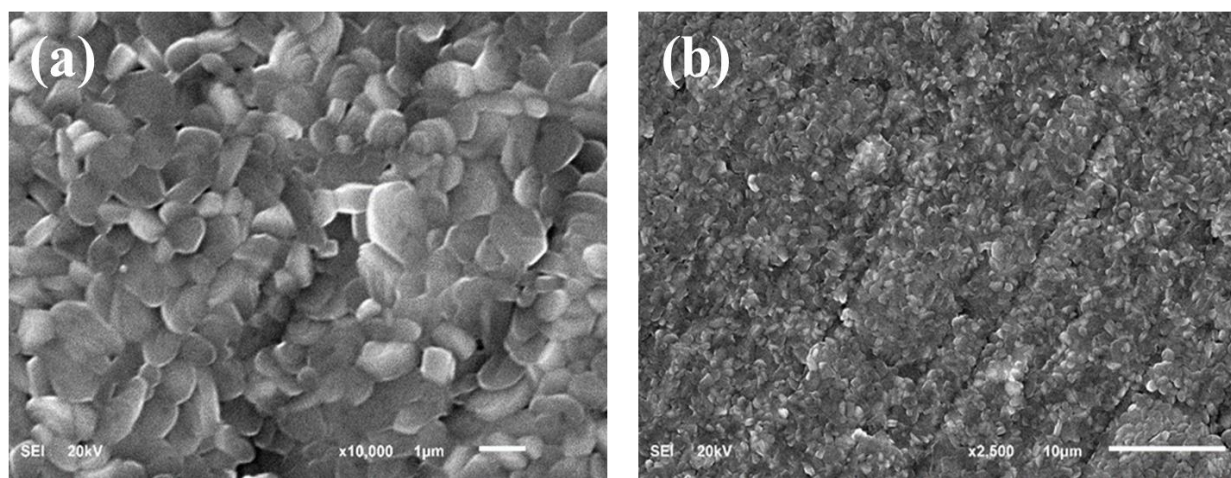


Figure 28: SEM images of two-dimensional (2D) layered of Vanadium oxides microflakes (2 μm V, 600 $^{\circ}\text{C}$) at two different magnification (a) 10,000 and (b) 2,500

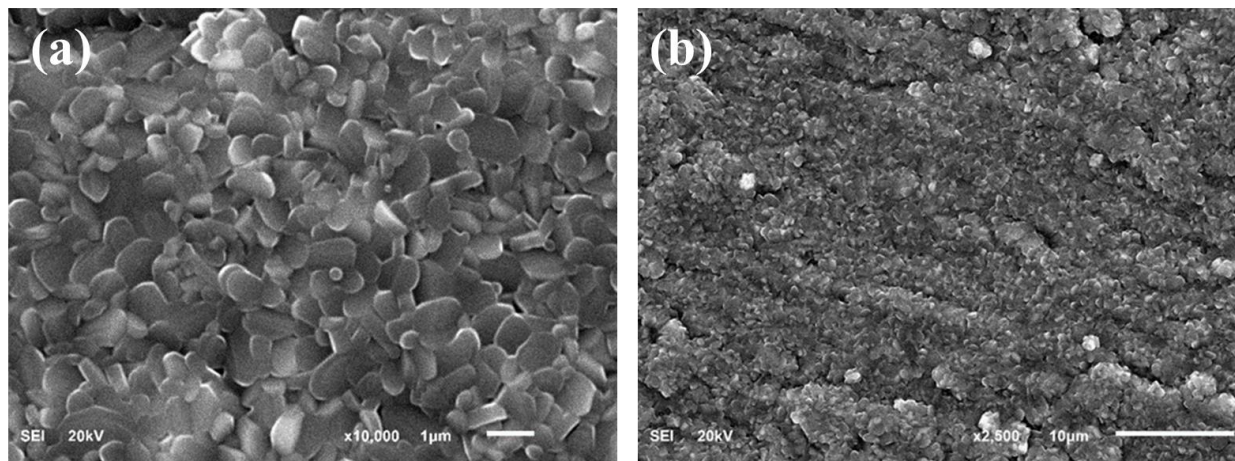


Figure 29: SEM images of two-dimensional (2D) layered of Vanadium oxides microflakes (1 μm V, 600 $^{\circ}\text{C}$) at two different magnification (a) 10,000 and (b) 2,500

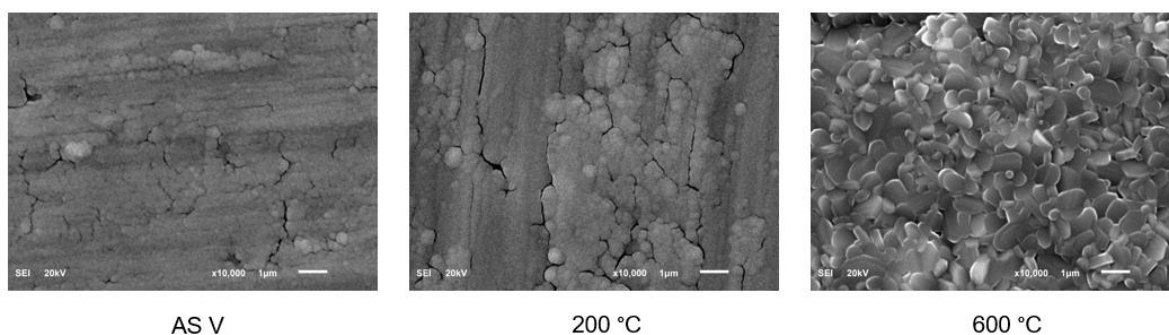


Figure 30: SEM images of two-dimensional (2D) layered Vanadium oxides thin film (AS deposited V, post-annealed at 200 $^{\circ}\text{C}$ and post-annealed at 600 $^{\circ}\text{C}$).

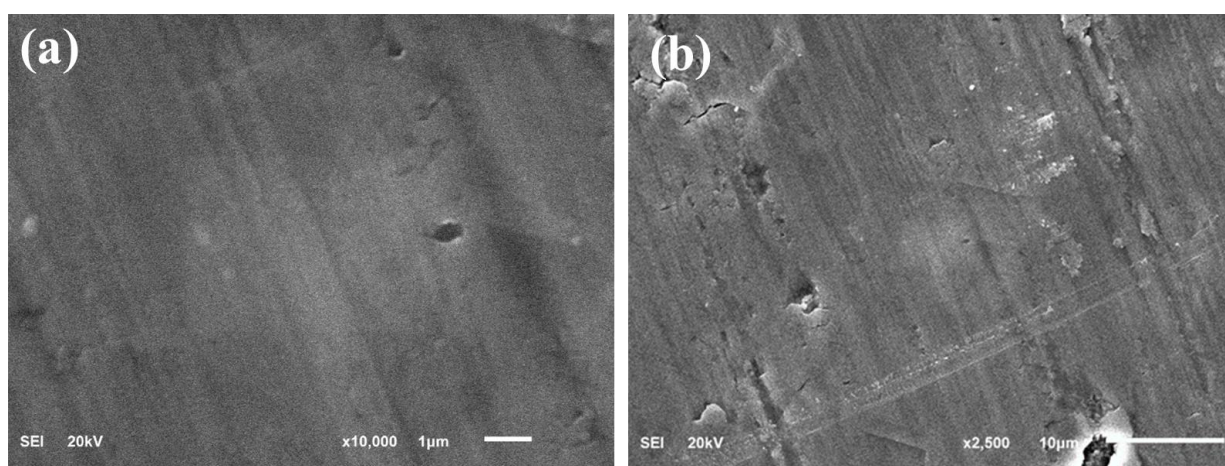


Figure 31: SEM images of two-dimensional (2D) layered vanadium oxides thin film (Sputtered with O_2) at two different magnification (a) 10,000 and (b) 2,500

4.1.3 Optical Profilometry

Optical profilometry is a non-contact surface measurement technique that is utilized to measure the thickness of thin films. Here, it is used to accurately measure the thickness of vanadium layer before oxidation as shown in Figure 32. The profilometer uses light to illuminate the sample surface and analyze reflected light to accurately find the thickness profile of thin film. Table 4 shows the results obtained from the profilometer measurements. Step measurements are taken at different locations on solid samples. The oxidation process exposed to different thickness samples result in different oxide thin films, and it is important to measure the thickness to understand the effect of the oxidation process on the layer.

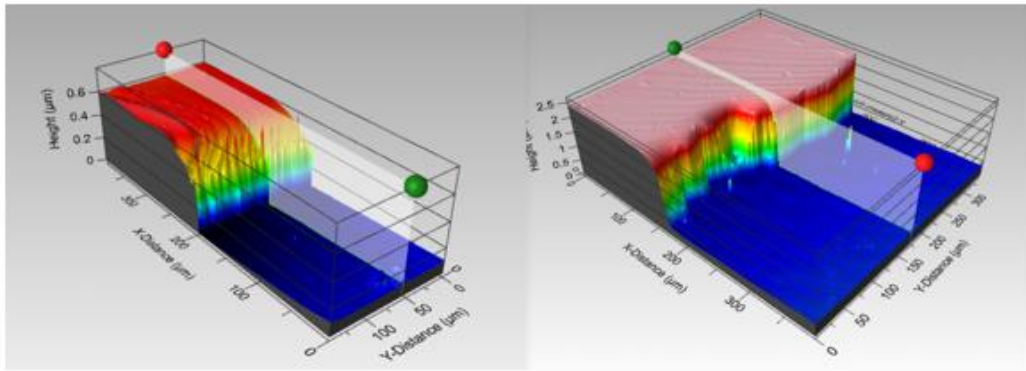


Figure 32: Optical Profilometry for sputtered Vanadium.

Table 4: Sputtering deposition time and layer thickness for vanadium oxide.

Vanadium Metal Total Deposition Time	Vanadium Metal Thickness by Optical Profilometer
1.5 hours	0.5 μm
3 hours	1 μm
6 hours	2 μm

4.2 Electrochemical Results

4.2.1 Cyclic Voltammetry

Cyclic voltammetry (CV) is used to measure the flow of current for electrochemical cells as a function of the applied voltage. The resultant CV curves can provide vital information regarding the electrochemical properties such as reaction kinetics, stability, and redox properties.

The V_2O_5 thin films have shown excellent discharging property. The electrochemical performances of the thin film V_2O_5 is evaluated as a cathode, Zn foil acting as anode, and the Zinc Sulfate $Zn(SO)_4$ electrolyte. V_2O_5 coated thin film on Ti foil via DC magnetron sputtering has been successfully tested in a typical cyclic voltammetry, and the charging and discharging capacity analysis have been carried out between a voltage window of 0.2V to 1.8V. Among all materials, the 1 μm deposited thin film V_2O_5 has shown the excellent results compared to other materials.

In general, there are two strong peaks around 1.2 to 0.9 V and 0.8 to 0.5 V in the CV data that directly indicate the intercalation and de-intercalation of Zn^{2+} into the V_2O_5 structure. In CV cycle, the peak position for 1 μm V_2O_5 materials is well defined, whereas the other two material peak position are not well defined. This indicates the intercalation of electrolyte into V_2O_5 structure for 1 μm thin film layer. Two different scan rates of 10 mVs and 100 mVs are used for annealed and sputtered cathode in presence of oxygen as shown in Figure 33 and Figure 34. Figure 35 shows CV voltammogram demonstrating the post-annealing temperature effect. The temperature effect is studied for the optimized condition (1 μm thickness, approach 1) Temperature conditions used are 200, 400 and 600 $^{\circ}C$.

For annealed samples involving DC sputtering of Vanadium oxide thin films as shown in Figure 33, 34 and 35, the CV curves exhibit the behavior of a capacitive cathode. The cathodic peak current and voltage increased with an increase in annealing temperature, indicating improvement in electrochemical activity. The anodic peak current is also found to increase with the increase in annealing temperature. This indicates that the thin film vanadium oxide layer may be susceptible to dissolution or degradation during charging and discharging. Figure 36 shows CV curves for different scan rates ranging from 10 mV to 100 mV. High scan rate leads to high integrated area and high capacitance due to increase in charge transfer at electrolyte/electrode interface. Moreover, the peak current values increased with the increase in scan rate. The results show that annealed thin film samples have better capacitance than sputtering carried out in the presence of oxygen. It

is important to note that the electrochemical performance of thin films is dependent on different factors including morphology, composition, sputtering conditions and film thickness as shown in SEM results that the interlining spaces observed in annealed vanadium oxide layers are desirable for intercalation and deintercalation of Zn ions during charging and discharging.[73]

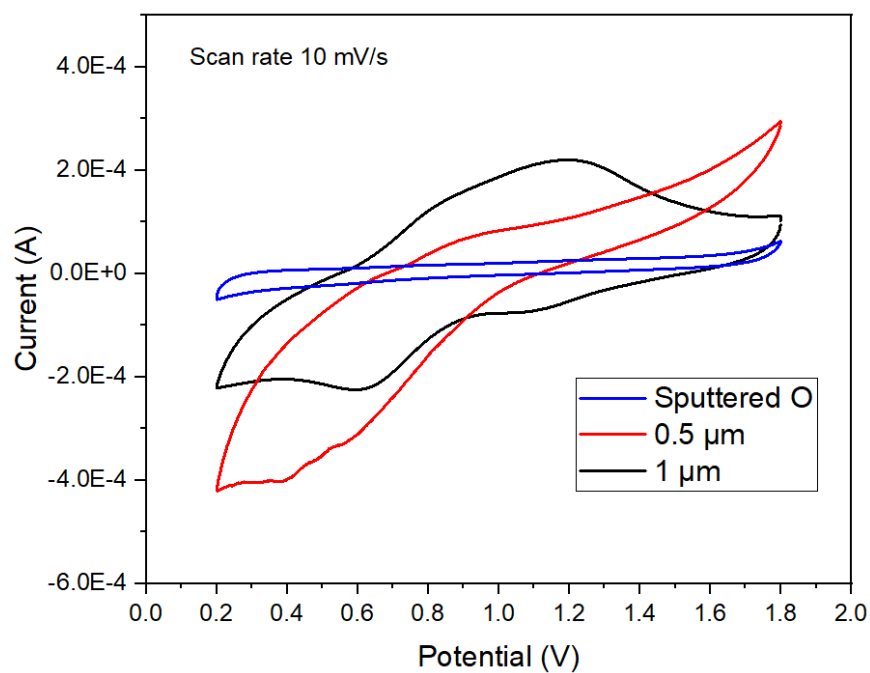


Figure 33: CV curves of V_2O_5 with different thickness of metal layer (approach 1), compared to sputtered with Oxygen (approach2) Scan rate 10 mV/S

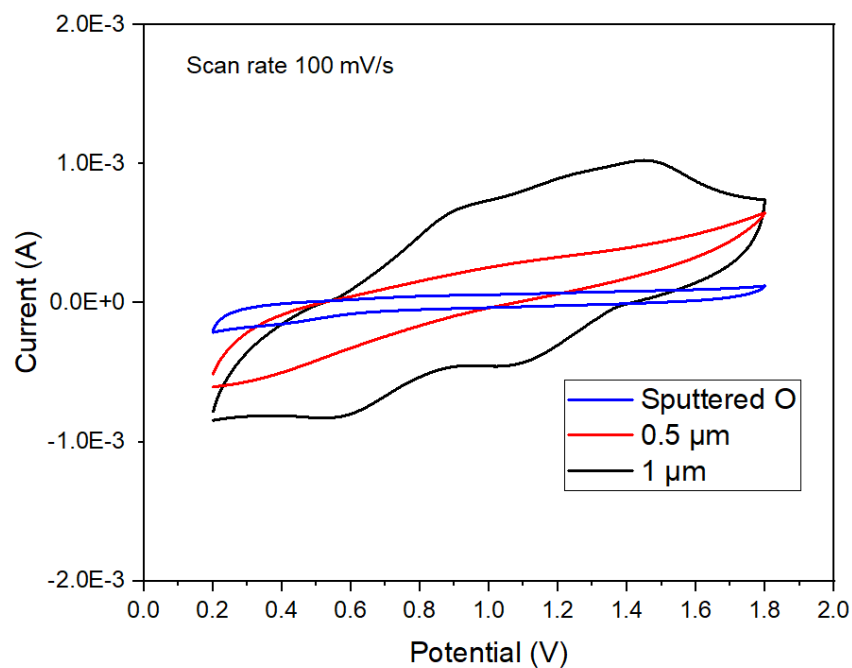


Figure 34: CV curves of V_2O_5 with different thickness of metal layer (approach 1), compared to sputtered with Oxygen (approach2). Scan rate 100 mV/S

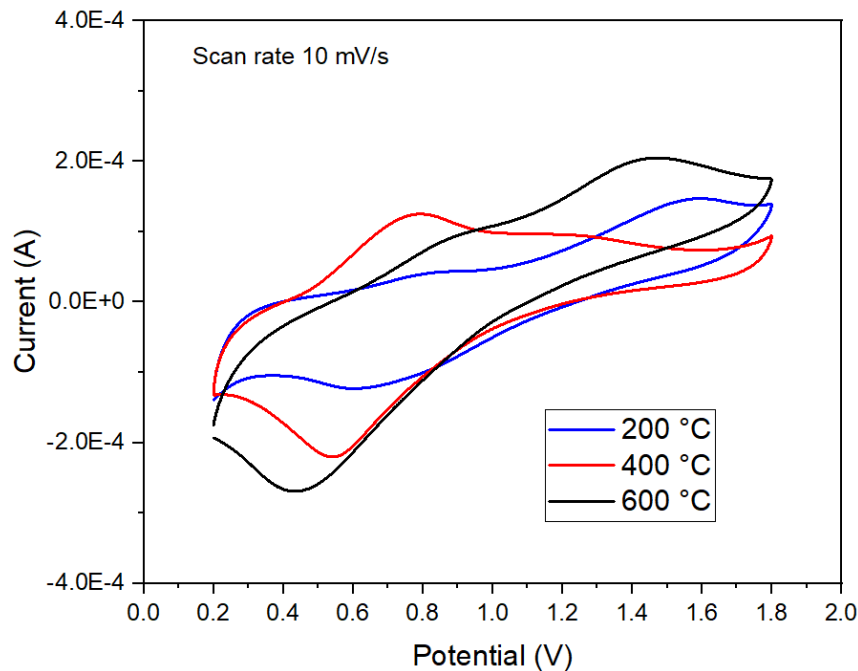


Figure 35: CV curves for annealed thin films at 200, 400 and 600 °C at scan rate of 10 mV/s for the optimized condition (1 μm, approach1)

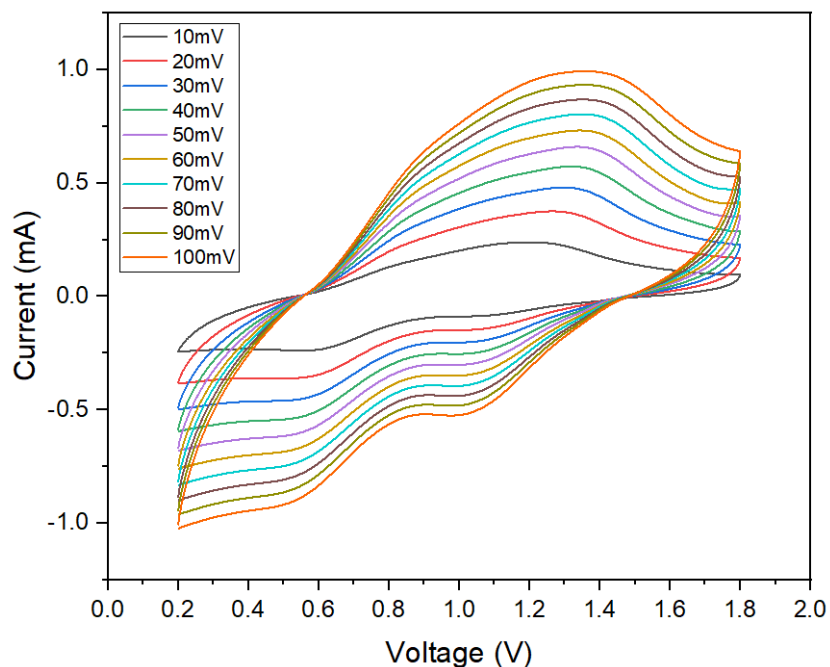


Figure 36: CV voltammogram for Vanadium oxide thin film at different scan rates. For the optimized condition (1 μm , 600 $^{\circ}\text{C}$)

4.2.2 Galvanostatic Charging Discharging (GCD)

The GCD curves for annealed samples and sputtered samples with oxygen gas are shown in figures 37 and 38. GCD analysis shows a decrease in potential over time, indicating discharging in the cell. The discharge process using GCD is divided into two main regions including an initial plateau during which the potential remains relatively constant. This region is followed by the area where potential decreases linearly and abruptly with time. The formation of two distinct regions is consistent with the literature. The first region is referred to as potential plateau. This region is associated with solid electrolyte interface. The second region is known as voltage drop region where voltage decreases linearly with time. This region gives information about discharge rate that is crucial to determine the performance of battery system.

For sputtered films with annealing, the discharge capacity is dependent on the thickness of the sputtered films. Generally, thicker films show high discharge capacities. Moreover, the annealing

temperature may lower the discharge capacity indicating that annealing at high temperature may lead to decrease in active material sites for the electrochemical reaction.

For the sputtering in the presence of oxygen gas as shown in figure 39, the discharge capacity seems to be constant and lower than for the annealed samples. The reason behind this is likely due to less thickness of the oxide film. In conclusion, GCD results show that annealed thin films and sputtered thin film in the presence of oxygen can be used to fabricate vanadium oxide thin film with good electrochemical performance. But the annealed thin film may be better suited for applications that require high discharge capacity, while the oxygen gas sputtered approach may be suited for such applications where thin films are required and simpler processing is preferred.[74]

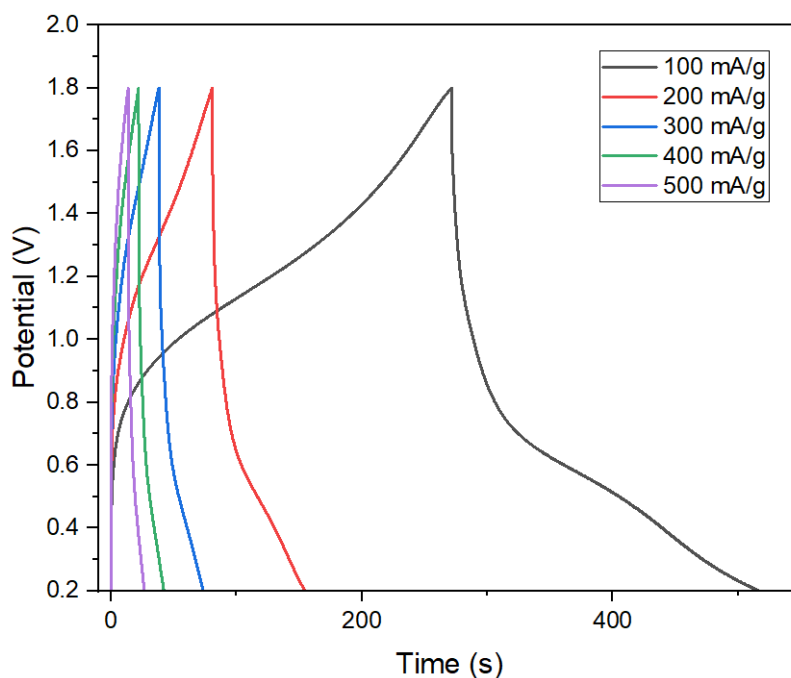


Figure 37: GCD analysis for Vanadium oxide thin film at different current densities. For the optimized condition (1 μm , 600 $^{\circ}\text{C}$)

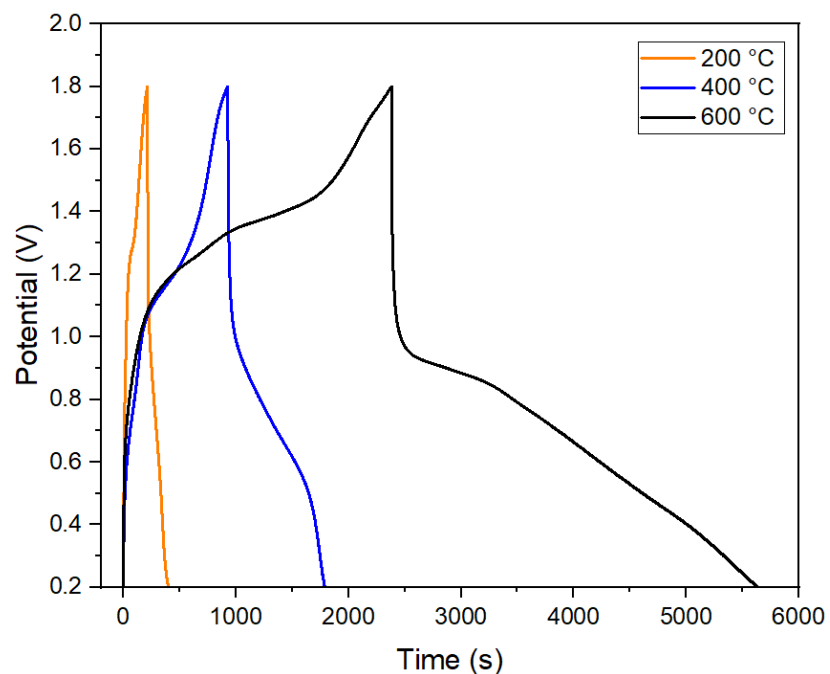


Figure 38: GCD analysis for Vanadium oxide post annealed at different temperature.

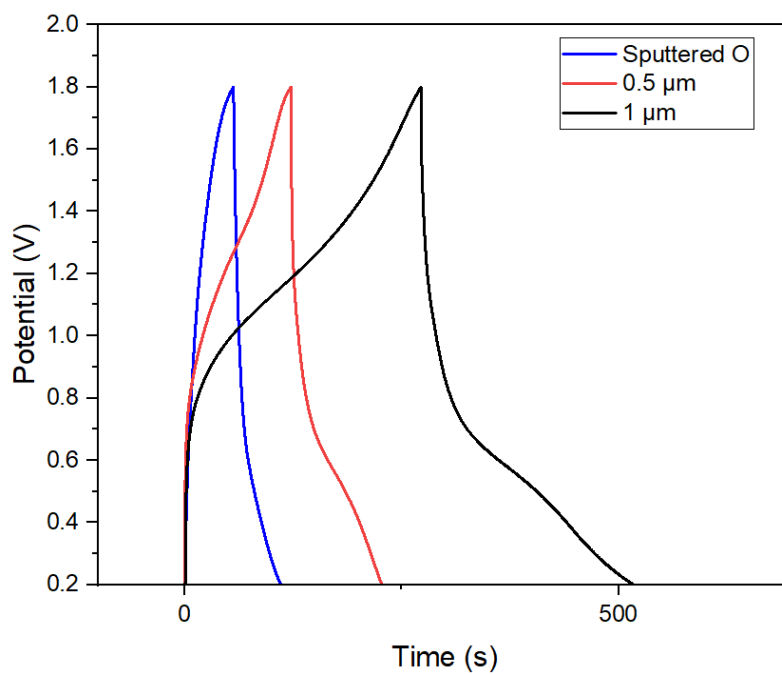


Figure 39: GCD analysis of Vanadium oxide with thickness of 0.5 and 1 microns at the optimized temperature (600 °C) and as-sputtered with O₂ gas (blue)

4.2.3 Electrochemical Impedance Spectroscopy (EIS)

EIS can provide important information regarding the capacitance and resistance of the cell, that are related to the performance and efficiency of the cell. EIS is used to study and analyze the effects of cycling for the impedance of the cell. The impedance is measured as the function of frequency and is plotted on a Nyquist plot, that shows the real part for the impedance (Z') along x-axis and the imaginary part for the impedance (Z'') along y-axis. EIS of optimized thickness is shown in Figure 40 before and after 500 charge/discharge cycles. The graph shows better performance for thin film before cycling likely due to better conductivity and less resistance to flow of electrons. The high impedance for the film after 500 cycles indicates a decrease in electrochemical activity.[75]

The second larger circle in the Nyquist plot for around 500 cycles shows an increase in impedance compared to the initial Nyquist plot due to decrease in electrochemical activity. This decrement can be associated with different factors including formation of a solid-electrolyte interface that can hinder ion transport and increase the resistance in electrodes. Other important factors that may contribute are degradation of active material during cycling and the formation of non-conductive passive layer on the electrode surfaces.

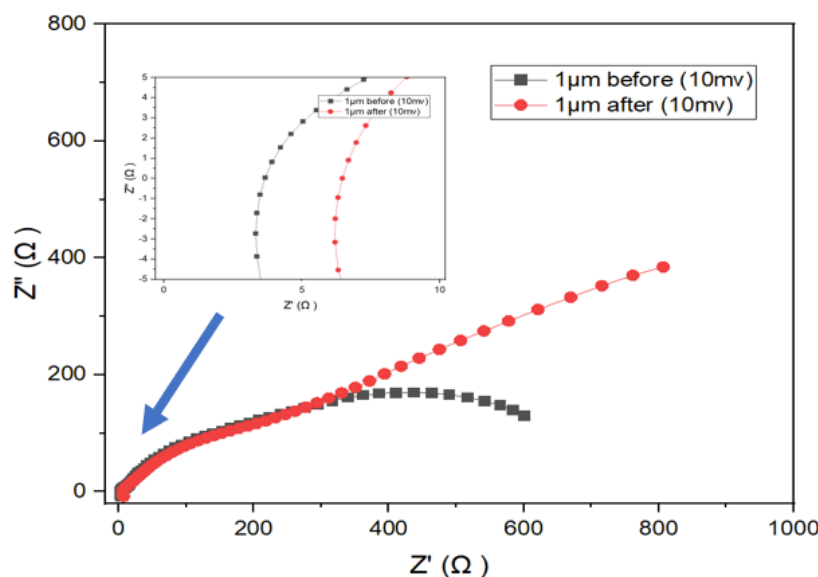


Figure 40: EIS of optimized condition of Vanadium Oxide before and after 500 charge/discharge cycles.

4.2.4 Discharge Specific Capacity

The discharge specific capacity test is used to analyze the performance and efficiency of electrochemical cells. This test analyzes the charge retention during each cycle and is known as the amount of charge per unit mass or volume for active material. The results are plotted as a graph of specific capacity at y-axis and the number of cycles at x-axis as shown in Figure 41. Annealed sample with 1 μm thickness shows the best specific capacity retention for first 50 cycles. The electrochemical activity starts to decrease after 50 cycles and stabilized. For oxygen sputtered sample, the result is completely opposite to the annealed samples. Figure 41 shows no charge retention and specific capacity for oxygen sputtered samples after the first 30 cycles.

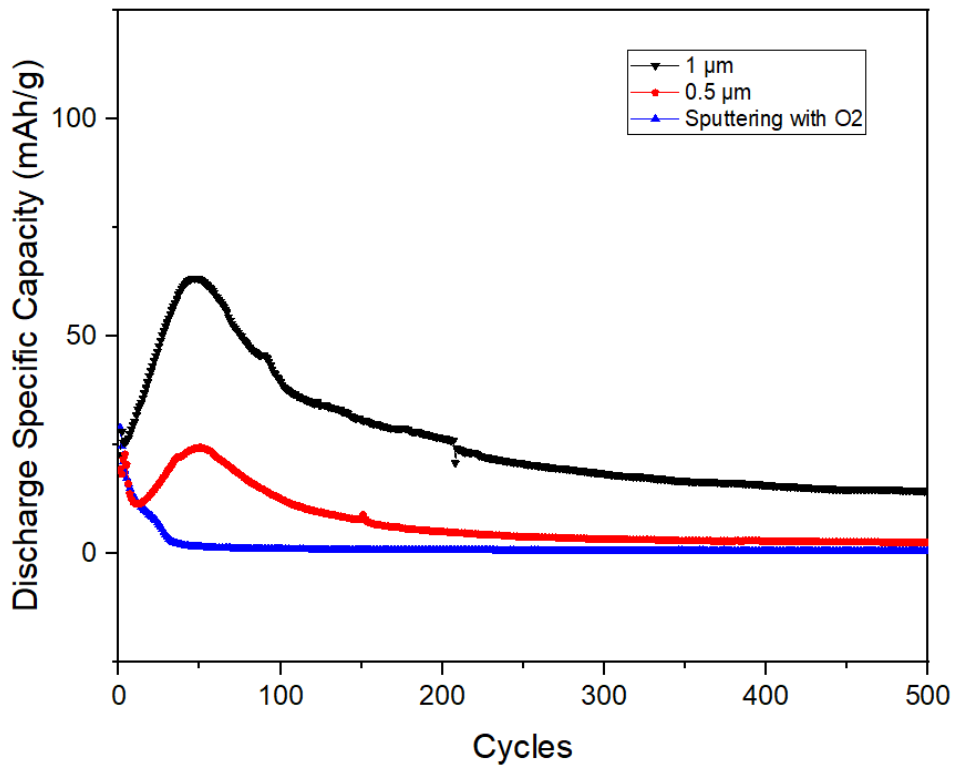


Figure 41: Discharge Specific Capacity for annealed samples of 0.5 and 1 micron and oxygen sputtered samples.

4.2.5 Degradation Mechanism

The cycling effect in the GCD results and other electrochemical results show that V_2O_5 layer in both annealed and oxygen sputtering thin film cathode samples in coin cell are prone to transfer material from the cathode on Ti foil to the anode on Zn foil and other parts of battery during cycling as shown in Figure 42. This process is known as cathode dissolution or material transfer. This material transfer of material can potentially affect the overall performance, efficiency, capacity loss and stability of the coin cell over longer cycling. It is, therefore, critical to analyze this issue by optimizing the electrode design to minimize the transfer of active materials and maintain long-term cyclic stability.

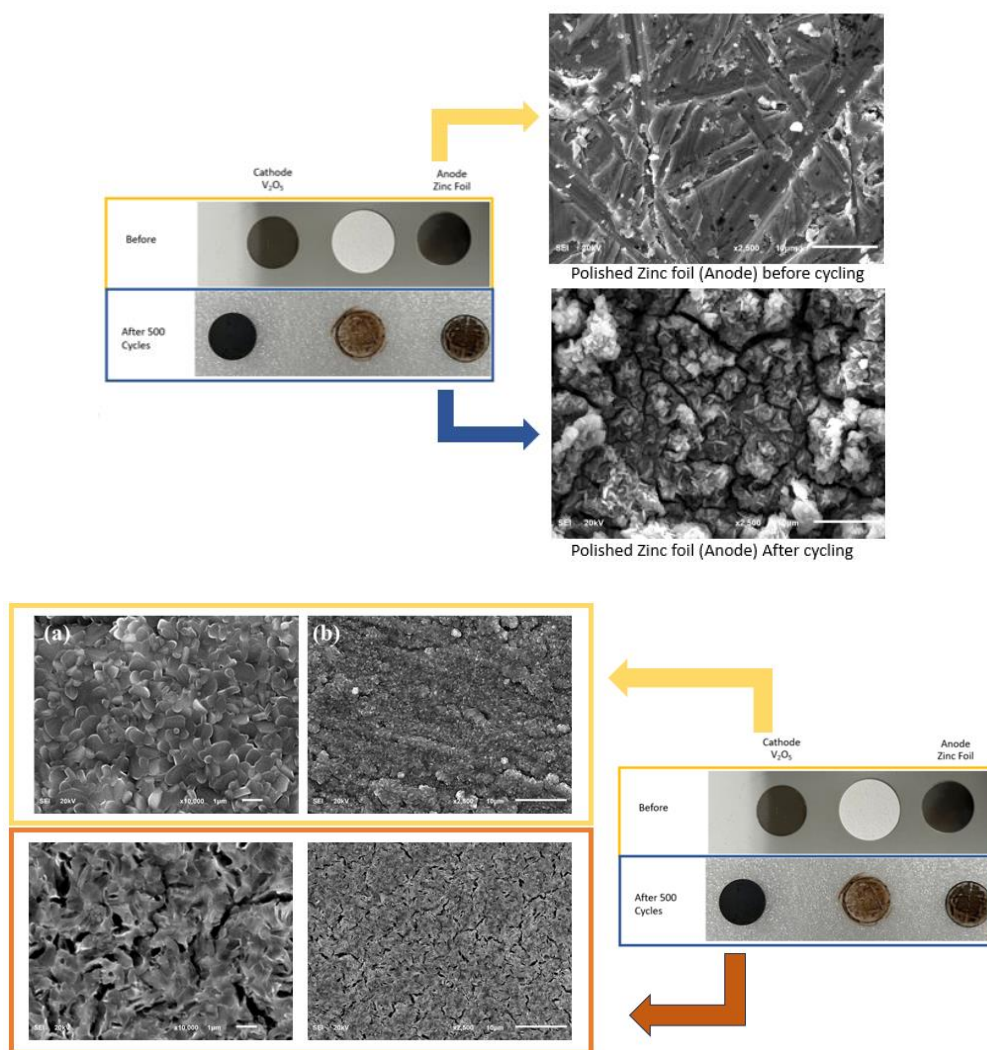


Figure 42: Degradation and material transfer of cathode material to anode.

Figure 43 shows the characteristic peaks for Zn foil anode before and after 500 cycles. XRD pattern shows the crystalline nature of Zn anode material. The additional peak in XRD pattern for the Zn anode after 500 cycles gives hint of degradation during cycling. In case of the zinc anode, a new peak is observed after 500 cycles possibly due to the indication of change in the state of V_2O_5 . Figure 44 shows XRD pattern for the cathode, V_2O_5 thin film cathode after annealing at 600 °C and vanadium oxide thin film cathode after 500 cycles. V_2O_5 characteristic peaks are also confirmed before and after cycling. It is observed that the intensity of characteristic peaks is decreased after cycling possibly due to decrease in crystallinity as a result of degradation. After 500 cycles, peaks are going to be more similar to that of Ti foil and only a few peaks matching to the reference V_2O_5 spectra.

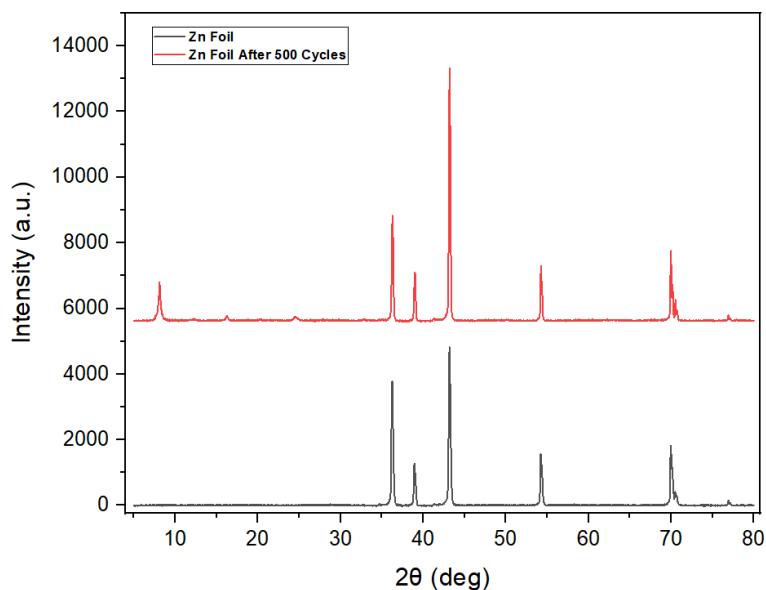


Figure 43: XRD pattern for Zn foil before and after 500 cycles.

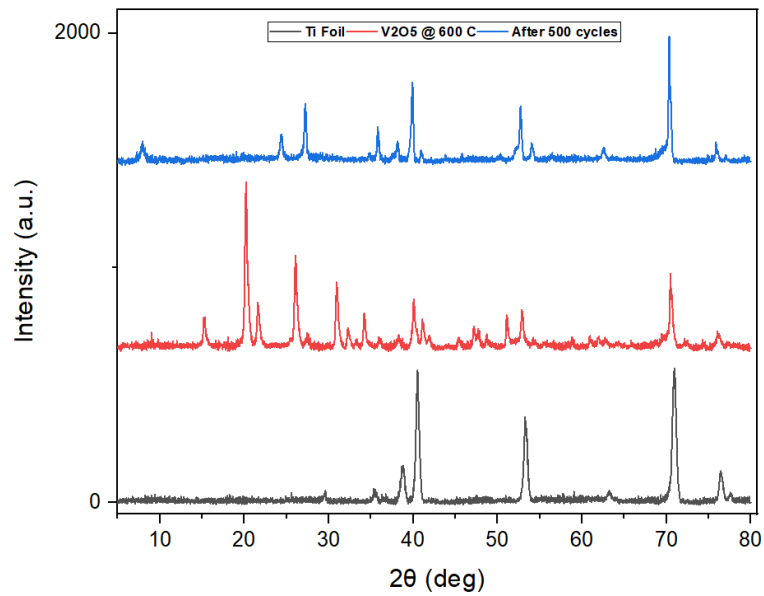


Figure 44: XRD pattern for Ti foil substrate, V_2O_5 at 600 °C annealing temperature after 500 cycles.

Chapter 5: Conclusion

5.1 Conclusion

This thesis has investigated two different methods to fabricate vanadium oxide thin film cathodes for use in zinc ion batteries specifically in coin cells. The first method involves DC sputtering of vanadium thin metal film on Ti foil for thicknesses of 0.5 μm , 1 μm and 2 μm that is followed by annealing in air at different temperatures to form the oxide layer. The second method involves the use of oxygen gas during sputtering process and does not need final annealing for oxide layer formation. The resulting vanadium oxide thin films are then evaluated using SEM, XRD, optical profilometry and various electrochemical techniques to compare the performance and efficiency of both methods.

The XRD analysis reveals the presence of main diffraction peaks for monolithic and crystalline V_2O_5 phase demonstrating the successful formation of oxidized layer in both methods. The identified diffraction peaks corresponding to the (110), (001), (021), and (020) planes for V_2O_5 crystal structure are clearly observed. Both fabrication methods exhibit the formation of crystalline V_2O_5 but the annealed thin films have higher crystallinity likely due to large crystallite growth of V_2O_5 particles and better crystallographic alignment. The comparison between these two methods in SEM results reveals that the vanadium oxide layer formation with oxygen gas gives better results in terms of uniform morphology, particle size and structure. Introduction of oxygen gas saves the additional time required for annealing. CV results for annealed samples exhibit the behaviour of a capacitive cathode. The cathodic peak current and voltage increased with an increase in annealing temperature, indicating improvement in electrochemical activity.

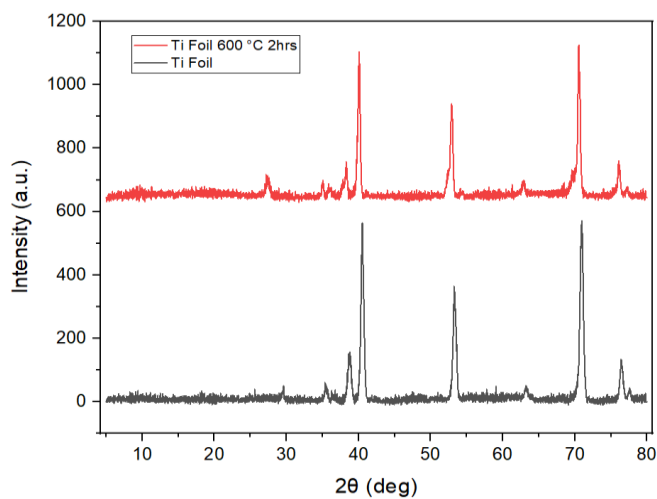
GCD analysis revealed that the discharge capacity of sputtered films with annealing is dependent on the thickness of the sputtered films. GCD results show that both methods can be used to fabricate vanadium oxide thin film with good electrochemical performance. But the annealed thin film may be better suited for applications that require high discharge capacity. The EIS graph shows better performance for thin film before cycling due to better conductivity and less resistance to flow of electrons. The high impedance for the film after 500 cycles indicates a decrease in electrochemical activity. Moreover, the transfer of vanadium oxide cathode material to the anode or other parts of coin cell is observed that requires further research to address the material dissolution and degradation over long-term cycling.

5.2 Future Recommendations

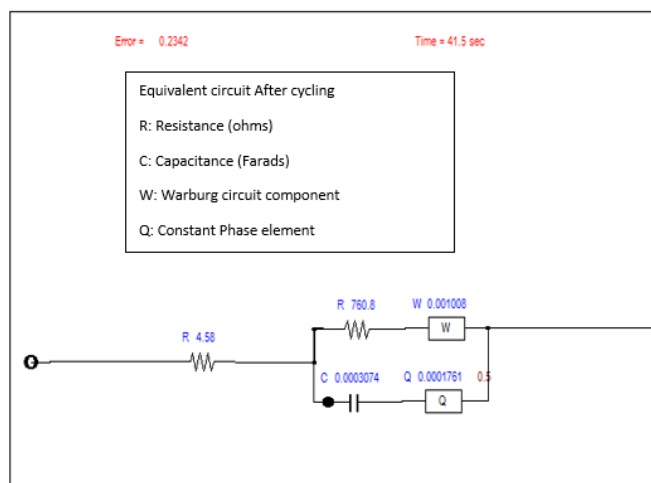
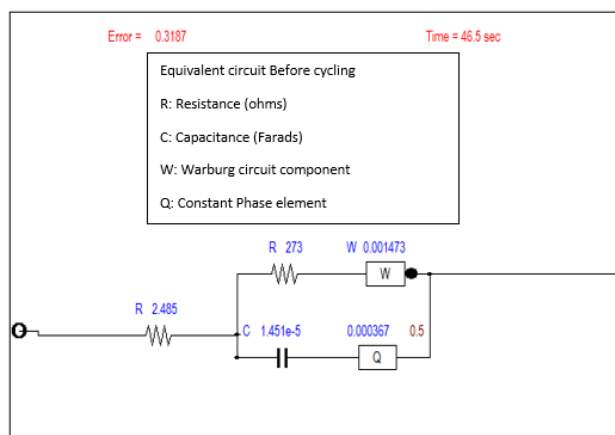
Several future recommendations can be considered and implemented to enhance performance efficiency and tap potential applications of ZIBs. The development of a passivation layer around zinc anode has many benefits. Passivation layer with optimized and tailored properties can address issues with stability and degradation of anode. Similarly, solid-state electrolytes present a wide range of properties that can be exploited. Aqueous electrolytes are commonly used but these solid-state electrolytes offer advantages including enhanced safety, wider operating temperature range, and high energy density. Research on the performance of solid-state electrolytes in ZIBs can lead to improved efficiency, performance, stability etc.

Another important aspect to consider is the utilization of 3D fabrication of cathode materials holds great potential to enhance the energy storage capacities of ZIBs. Further research is needed for these recommendations that will aid in optimizing the required properties and include new fabrication techniques. It is crucial to study scalability and cost evaluation before implementation. Research studies are focusing on developing highly efficient, stable, and cost-effective ZIBs for future energy storage devices based on these recommendations.

Appendix



XRD of Ti Foil before and after 2 hours of air annealing at 600 °C



Equivalent circuit of EIS results before and after 500 cycles of the optimized thin film condition

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