DESIGN, DEVELOPMENT, AND SCALE-UP OF AN ECONOMICAL AND EFFICIENT VANADIUM REDOX FLOW BATTERY

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by

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Submitted

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Dedicated

to my beloved family, my respected teachers, my dear friends, and to all the experiences found along the way

Maximum effort!

CERTIFICATE

This is to certify that the work carried out in this Ph.D. thesis entitled "**DESIGN, DEVELOPMENT, AND SCALE-UP OF AN ECONOMICAL AND EFFICIENT VANADIUM REDOX FLOW BATTERY**" submitted by Mr. Nishant Beriwal to the Indian Institute of Technology Delhi, for the fulfilment of the requirements for the award of Doctor of Philosophy in Chemical Engineering is a record of bonafide research work carried out by him. I certify that he has carried out this work under my supervision. The research work is original, and this work has not been submitted elsewhere in part or full, to any other university or institute for the award of any degree or diploma. Also, the material obtained from other sources has been acknowledged in the thesis.

Dr. Anil Verma
Professor

Date: 17.04.2025
Place: IIT Delhi

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STATEMENT

I, Nishant Beriwal, do hereby declare that this Ph.D. thesis entitled "**DESIGN, DEVELOPMENT, AND SCALE-UP OF AN ECONOMICAL AND EFFICIENT VANADIUM REDOX FLOW BATTERY**" is an original work carried out by me under the guidance and supervision of Prof. Anil Verma in the Department of Chemical Engineering, Indian Institute of Technology Delhi, Hauz Khas, New Delhi, India and is submitted to Indian Institute of Technology Delhi, Hauz Khas, New Delhi, India for the award of the degree of Doctor of Philosophy.

The interpretations put forth are based on my learnings and understandings of the original text and are not submitted, in part or full, to any other university or institute for the award of any degree or diploma. I also certify that the details and information taken from the works of other investigators, articles and websites which I have made use of are duly acknowledged at the respective place in this thesis.

Nishant Beriwal
Entry number: 2018CHZ2503

Date: **17.04.2025**
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(Nishant Beriwal)

Abstract

The intermittency of renewable energy sources can be tackled by integration with energy storage systems (ESS), which should be economical, efficient and suitable for large-scale energy storage. Vanadium redox flow battery (VRFB) has been emerging as one of the best ESS for its integration with renewable energy sources such as solar and wind power. Nevertheless, for an effective market penetration of any new technology, the capital cost is an extremely important factor. VRFB suffers from high capital costs primarily due to the high cost of vanadium electrolyte, arising from an expensive vanadium precursor (vanadyl sulfate, $VOSO_4$) used conventionally. In the first study, vanadium pentoxide (V_2O_5) is explored as an alternate vanadium precursor primarily due to its low-cost and common availability. However, the solubility of V_2O_5 is very low in H_2SO_4 solutions (~0.4 M VO_2^+ in 3 M H_2SO_4 at 40°C), which makes it impractical for preparing vanadium electrolytes of desired concentration (1.5 – 1.6 M V^{n+} in 4 M total sulfate). To tackle this challenge, a novel electrochemical synthesis route is developed which results in synthesis of desired vanadium electrolytes from V_2O_5. The synthesized electrolytes show similar performance to that of conventionally used $VOSO_4$ based electrolyte. Moreover, the economic analysis suggests more than 95% reduction in the cost of electrolyte synthesis using the developed process over conventional process, which would ultimately bring down the capital cost of kW-MW VRFB installations. Nevertheless, the availability of V_2O_5 could pose a serious threat to the supply-chain for VRFB applications since more than 95% of global annual production of V_2O_5 is utilized in metallurgical and catalyst industries. Furthermore, the production of V_2O_5 cannot be scaled-up since it is a co-product of iron and titanium mining from V-bearing titanoferrous magnetite ores (primary sources). In the

second study, waste vanadium sources such as spent vanadium catalysts (SVC) are explored as secondary vanadium sources for synthesizing vanadium electrolytes. However, the presence of variety of impurities (Na, K, Al, Fe, Cs, Mg, Ti, Ca, Zn, and Ni) makes it impractical for synthesizing vanadium electrolytes. To tackle this challenge, a novel vanadium extraction process is developed which resulted in extraction of direct-use V_2O_4 and V_2O_3 vanadium precursors. The electrolytes synthesized from these extracted vanadium powders result in similar performance to that of commercial electrolytes. Further, economic analysis is done to evaluate the commercial feasibility of the developed process. The cost of electrolyte synthesis using extraction route is around 2.73 $/L, which is significantly lower than reported V_2O_5 routes (~5.27 $/L). Lastly, a multi-cell VRFB system is designed and developed based on plate and frame design, where shunt currents are found to be a major performance loss parameter. The link between high shunt currents and associated bipolar plate degradation is established successfully, which is not reported anywhere in the literature. This novel finding is used to optimize the design and performance of a multi-cell VRFB system.

Keywords: Electrolyte; Extraction; Flow battery; Multi-cell stack; Spent vanadium catalyst; Shunt current; Vanadium.

सारांश

नवीकरणीय ऊर्जा स्त्रोतों की अंतरविरोधिता को ऊर्जा भंडारण प्रणालियों (ESS) के साथ एकीकृत करके हल किया जा सकता है, जो आर्थिक, कुशल और बड़े पैमाने पर ऊर्जा भंडारण के लिए उपयुक्त होनी चाहिए। वैनाडियम रेडॉक्स फ्लो बैटरी (VRFB) नवीकरणीय ऊर्जा स्त्रोतों जैसे कि सौर और पवन ऊर्जा के साथ एकीकरण के लिए सबसे उपयुक्त ESS के रूप में उभर कर सामने आई है। हालांकि, किसी भी नई तकनीकी के प्रभावी बाजार में प्रवेश के लिए पूंजी लागत एक अत्यंत महत्वपूर्ण कारक होती है। VRFB उच्च पूंजी लागत से ग्रस्त है, जो मुख्य रूप से वैनाडियम इलेक्ट्रोलाइट की उच्च लागत के कारण होती है, जो परंपरागत रूप से महंगे वैनाडियम अग्रणी (वैनाडाइल सल्फेट, $VOSO_4$) से उत्पन्न होती है। पहले अध्ययन में, वैनाडियम पेंटॉक्साइड (V_2O_5) को एक वैकल्पिक वैनाडियम अग्रणी के रूप में अन्वेषित किया गया है, मुख्य रूप से इसकी कम लागत और सामान्य उपलब्धता के कारण। हालांकि, V_2O_5 की घुलनशीलता H_2SO_4 समाधानों में बहुत कम है (~0.4 M VO_2^+ 3 M H_2SO_4 में 40 °C पर), जिससे यह वांछित सांद्रता (1.5 – 1.6 M V^{n+} 4 M कुल सल्फेट में) के वैनाडियम इलेक्ट्रोलाइट्स तैयार करने के लिए अव्यावहारिक बन जाता है। इस चुनौती से निपटने के लिए, एक नवीनतम इलेक्ट्रोकेमिकल संश्लेषण मार्ग विकसित किया गया है, जो V_2O_5 से वांछित वैनाडियम इलेक्ट्रोलाइट्स का संश्लेषण करता है। संश्लेषित इलेक्ट्रोलाइट्स परंपरागत $VOSO_4$ आधारित इलेक्ट्रोलाइट्स के समान प्रदर्शन दिखाते हैं। इसके अतिरिक्त, आर्थिक विश्लेषण से यह संकेत मिलता है कि विकसित प्रक्रिया के माध्यम से इलेक्ट्रोलाइट संश्लेषण की लागत में परंपरागत प्रक्रिया की तुलना में 95% से अधिक की कमी आएगी, जिससे kW-MW VRFB प्रतिष्ठानों की पूंजी लागत में कमी आएगी। फिर भी, V_2O_5 की उपलब्धता VRFB अनुप्रयोगों के लिए आपूर्ति श्रृंखला के लिए एक गंभीर खतरा उत्पन्न कर सकती है, क्योंकि विश्व उत्पादन का 95% से अधिक V_2O_5 धातुकर्म और उत्प्रेरक उद्योगों में उपयोग होता है। इसके अलावा, V_2O_5 का उत्पादन बढ़ाया नहीं जा सकता है क्योंकि यह लौह और टाइटेनियम खनन से उत्पन्न एक सह-उत्पाद है। दूसरे अध्ययन में, व्यर्थ वैनाडियम स्त्रोतों जैसे कि व्यर्थ वैनाडियम उत्प्रेरकों (SVC) का अन्वेषण किया गया है, जो वैनाडियम इलेक्ट्रोलाइट्स के संश्लेषण के लिए द्वितीयक वैनाडियम स्त्रोत के रूप में काम आ

सकते हैं। हालांकि, विभिन्न अशुद्धियों (Na, K, Al, Fe, Cs, Mg, Ti, Ca, Zn और Ni) की उपस्थिति इसे वैनाडियम इलेक्ट्रोलाइट्स के संश्लेषण के लिए अव्यावहारिक बना देती है। इस चुनौती से निपटने के लिए, एक नवीन वैनाडियम निष्कर्षण प्रक्रिया विकसित की गई है, जिसके परिणामस्वरूप सीधे उपयोग के लिए V_2O_4 और V_2O_3 वैनाडियम अग्रणी का निष्कर्षण हुआ। इन निष्कर्षित वैनाडियम पाउडरों से संश्लेषित इलेक्ट्रोलाइट्स वाणिज्यिक इलेक्ट्रोलाइट्स के समान प्रदर्शन करते हैं। इसके अलावा, विकसित प्रक्रिया की व्यावसायिक व्यवहार्यता का मूल्यांकन करने के लिए आर्थिक विश्लेषण किया गया है। निष्कर्षण मार्ग का उपयोग करके इलेक्ट्रोलाइट संश्लेषण की लागत लगभग 2.73 डॉलर/लीटर है, जो V_2O_5 मार्गों (~5.27 डॉलर/लीटर) की तुलना में काफी कम है। अंत में, एक बहु-कोशिका VRFB प्रणाली को प्लेट और फ्रेम डिजाइन के आधार पर डिज़ाइन और विकसित किया गया है, जहां शंट करेंट्स (shunt currents) को एक प्रमुख प्रदर्शन हानि कारक के रूप में पाया गया है। उच्च शंट करेंट्स और संबंधित बाइपोलर प्लेट के क्षय के बीच लिंक को सफलतापूर्वक स्थापित किया गया है, जो पहले कहीं भी रिपोर्ट नहीं किया गया था। इस नवीनतम खोज का उपयोग करके बहु-कोशिका VRFB प्रणाली के डिजाइन और प्रदर्शन को अनुकूलित किया गया है।

मुख्य शब्द: इलेक्ट्रोलाइट; निष्कर्षण; फ्लो बैटरी; बहु-कोशिका स्टैक; व्यर्थ वैनाडियम उत्प्रेरक; शंट करेंट्स; वैनाडियम।

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List of Abbreviations

AMV	Ammonium metavanadate
COP	Conference of the Parties
CE	Coulombic efficiency
CNC	Computerized numerical control
CRF	Central Research Facility
CV	Cyclic voltammetry
DC	Direct current
DI	De-ionized
EE	Energy efficiency
EDX	Energy dispersive X-ray
ESS	Energy storage system
EU	Electrolyte utilization
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared
GF	Graphite felt
GW	Giga Watt
HER	Hydrogen evolution reaction
ICPMS	Inductively coupled plasma mass spectrometry
IPA	Isopropanol alcohol
JCPDS	Joint Committee on Powder Diffraction Standards
kW	Kilo Watt
LAB	Lead acid battery
LCoE	Levelized cost of energy
LIB	Lithium-ion battery

MOC	Material of construction
MNRE	Ministry of New and Renewable Energy
MW	Mega watt
OCV	Open circuit voltage
OER	Oxygen evolution reaction
PAN	Polyacrylonitrile
Pt/C	Platinum supported on carbon
PV	Photovoltaic
PVDF	Polyvinylidene difluoride
RFB	Redox flow battery
S/L	Solid to liquid ratio
SEM	Scanning electron microscopy
SERL	Sustainable Environergy Research Lab
SHE	Standard hydrogen electrode
SoC	State-of-charge
SoH	State-of-health
SVC	Spent vanadium catalyst
TGF	Thermally-treated graphite felt
UNFCCC	UN Framework Convention on Climate Change
UV-vis	Ultra-violet visible
VE	Voltage efficiency
VP	Vanadium pentoxide
VRFB	Vanadium redox flow battery
VS	Vanadyl sulfate
XRD	X-ray diffraction

List of Nomenclatures

$\mathbf{C_c}$	Charge capacity (Ah/L)
$\mathbf{C_d}$	Discharge capacity (Ah/L)
$\mathbf{C_{cat}}$	Cost of Pt/C catalyst ($)
$\mathbf{C_E}$	Cost of energy ($)
$\mathbf{C_{electrolyte}}$	Concentration of vanadium electrolyte (mol/L)
$\mathbf{C_{H2}}$	Cost of H_2 gas ($)
$\mathbf{C_{V2O5}}$	Cost of V_2O_5 ($)
$\mathbf{C_{VP}}$	Cost of synthesis of VP electrolyte ($)
$\mathbf{C_{VOSO4}}$	Cost of $VOSO_4$ ($)
$\mathbf{C_{VP}^S}$	Cost of supporting electrolyte for VP electrolyte synthesis ($)
$\mathbf{C_{VS}^S}$	Cost of supporting electrolyte for VS electrolyte synthesis ($)
$\mathbf{C_{leached}^V}$	Concentration of leached vanadium stock (mol/L)
$\mathbf{C_{VS}}$	Cost of synthesis of VS electrolyte ($)
$\mathbf{E^0}$	Standard reduction potential (V)
$\mathbf{E_{anode}^0}$	Standard anode reduction potential (V)
$\mathbf{E_{cathode}^0}$	Standard cathode reduction potential (V)
$\mathbf{E_{cell}^0}$	Standard cell reduction potential (V)
$\mathbf{E_p^a}$	Peak anodic potential (V)
$\mathbf{E_p^c}$	Peak cathodic potential (V)
$\mathbf{\Delta E_p}$	Peak potential separation (V)
$\mathbf{E_{ext,V}}$	Electrolytes synthesized using extracted vanadium
$\mathbf{E_{o/r}}$	Energy input in oxidation/reduction step (Ah)
$\mathbf{E_{ox}}$	Energy input in oxidation step (Ah)
$\mathbf{E_{red}}$	Energy input in reduction step (Ah)

$\mathbf{E_{std,V}}$	Standard vanadium electrolytes
$\mathbf{F}$	Faraday's constant (C/mol)
$\mathbf{I_{pa}}$	Peak anodic current (mA)
$\mathbf{I_{pc}}$	Peak cathodic current (mA)
$\mathbf{M^{W}_{V2O5}}$	Mol. wt. of V_2O_5 (g/mol)
$\mathbf{m_{cat}}$	Mass of 40 wt.% Pt/C catalyst (g)
$\mathbf{m_{SVC}}$	Mass of SVC (kg)
$\mathbf{m_{VP}}$	Mass of vanadium pentoxide (kg)
$\mathbf{m_{VS}}$	Mass of vanadyl sulfate (kg)
$\mathbf{M_{V(V)}}$	Molarity of V*(V)* ions (mol/L)
$\mathbf{n_{H2}}$	Number of moles of H_2 gas
$\mathbf{n_{L}}$	Number of moles of H_2 gas
$\mathbf{P_{cat}}$	Price of 40 wt.% Pt/C catalyst ($/g)
$\mathbf{P_{E}}$	Price of energy ($/Ah)
$\mathbf{P_{H2}}$	Price of hydrogen gas ($/mol)
$\mathbf{P_{SVC}}$	V_2O_5 content detected in SVC (%)
$\mathbf{P_{VP}}$	Price of 99% vanadium pentoxide ($/kg)
$\mathbf{P_{VS}}$	Price of 96% vanadyl sulfate ($/kg)
$\mathbf{P_{W}}$	Price of DI water ($/L)
$\mathbf{V^{3.5+}}$	Equimolar mix of VO^{2+} and V^{3+}
$\mathbf{V^{L}_{3M-SA}}$	Volume of 3 M H_2SO_4 in leaching step (L)
$\mathbf{V^{pH}_{3M-SA}}$	Volume of 3 M H_2SO_4 in pH alteration step (L)
$\mathbf{V^{t}_{3M-SA}}$	Total volume of 3 M H_2SO_4 used (L)
$\mathbf{V^{pH4}_{0.6-AH}}$	Volume of 0.4C NH_4OH in pH alteration to 4 (L)
$\mathbf{V^{pH7}_{0.6-AH}}$	Volume of 0.4C NH_4OH in pH alteration to 7 (L)
$\mathbf{V^{t}_{0.6-AH}}$	Total volume of 0.4C NH_4OH used (L)

$\mathbf{V_{4M-SA}}$	Volume of 4 M H_2SO_4 (L)
$\mathbf{V_c^i}$	Initial charge voltage (V)
$\mathbf{V_d^i}$	Initial discharge voltage (V)
$\mathbf{V_c^f}$	Final charge voltage (V)
$\mathbf{V_d^f}$	Final discharge voltage (V)
$\mathbf{V_{VP}^{II}}$	Volume of VP based V*(II)* electrolyte (L)
$\mathbf{V_{VP}^{3.5}}$	Volume of VS based $V^{3.5+}$ electrolyte (L)
$\mathbf{V_{VP}^{V}}$	Volume of VP based V*(V)* electrolyte (L)
$\mathbf{V_{VS}^{II}}$	Volume of VS based V*(II)* electrolyte (L)
$\mathbf{V_{VS}^{IV}}$	Volume of VS based V*(IV)* electrolyte (L)
$\mathbf{V_{VS}^{V}}$	Volume of VS based V*(V)* electrolyte (L)
$\mathbf{V_{electrolyte}}$	Volume of electrolyte (L)
$\mathbf{V_M}$	Volume of Mohr's salt (mL)
$\mathbf{V_{SA}}$	Volume of 98% sulfuric acid (L)
$\mathbf{V_W}$	Volume of DI water (L)
$\mathbf{x_E}$	Fraction of vanadium extracted in vanadium extraction step
$\mathbf{x_{IR}}$	Fraction of vanadium preserved in impurity removal step
$\mathbf{x_L}$	Fraction of vanadium leached in leaching step