DEVELOPMENT OF EFFICIENT AND DURABLE VANADIUM REDOX FLOW BATTERY

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DEVELOPMENT OF EFFICIENT AND DURABLE VANADIUM REDOX FLOW BATTERY

by

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Submitted

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CERTIFICATE

This is to certify that the work contained in this thesis entitled "**DEVELOPMENT OF EFFICIENT AND DURABLE VANADIUM REDOX FLOW BATTERY"** submitted by Mr. Manshu Kapoor to the Indian Institute of Technology Delhi, for the fulfillment 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. Moreover, the material obtained from other sources has been duly acknowledged in the thesis.

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STATEMENT

I do hereby declare that this Ph.D. thesis entitled “**DEVELOPMENT OF EFFICIENT AND DURABLE 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 readings 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 acknowledged at the respective place in this thesis.

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For me, pursuing research was an intuitive decision and it was some day in 2016 on which I decided that I will quit my job and commit myself towards a research-oriented career. In 2017, I was fortunate enough to join the Chemical Engineering Department of IIT Delhi as a Ph.D. Research Scholar and since then, I dedicated every bit of mine towards my project in an intention to justify myself and at the same time serve the nation. The research work presented in this thesis would have not been possible without the support of several people. Therefore, I take this opportunity to acknowledge everyone with whose support I was able to complete my Ph.D. thesis.

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(Manshu Kapoor)

Abstract

Intermittent nature of the renewable energy sources dictates the need to develop a reliable and sustainable energy storage technology. Among various available technologies, vanadium redox flow battery (VRFB) is one of the best suited technologies for large-scale/stationary electrical energy storage application. VRFB has the capability to undergo a large number of charge-discharge cycles (~ 20,000) and allows the decoupled scaling of power and energy. However, the widespread commercialization of VRFB is still hindered because of certain challenges. The first challenge is associated with development of efficient electrode material for VRFB. Currently, graphite felt (GF) is a widely used electrode material for VRFB. However, it has been observed that bare GF performs inefficiently in VRFB and hence electrode pre-treatment is necessary. Currently, the available pre-treatment procedures are either complex or non-viable to be executed for large electrodes. Therefore, this thesis presents a tactical procedure to pre-treat the GF. The pre-treated electrode possesses large surface area, well-developed uniform pore structures, and abundant oxygen-rich surface functional groups. The simple and tactical pre-treatment approach followed in this thesis improves the peak power density of GF to 350 $mW \cdot cm^{-2}$ (3-fold increase from bare GF). The subsequent challenges are related to the technological obstacles observed during the operation of VRFB. It is known that during operation of VRFB, the vanadium species crossover across the ion exchange membrane (IEM). As a result, the phenomenon of capacity fade and self-discharge come into picture. To tackle capacity-fade, this thesis addresses a unique electrolyte repair point (ERP) which is a logical tool to identify right time for the electrolyte repair during operation of VRFB. Subsequently, on basis of ERP a smart electrolyte health management system was devised that was capable to ensure the durability and efficiency of the VRFB. Like capacity-fade, the self-discharge process is also closely linked to complex movement of vanadium species across IEM and substantial amount of energy is lost during the process. To address this concern, this study observed the self-discharge process in VRFB with the help of carefully designed experiments. Further, to generalize the understanding derived from the experiments a mathematical model was developed. The developed mathematical model successfully predicts the self-discharge time of VRFB within an error of ~ ±10% and on basis of the efficacy of the model a case-study on a kW-scale VRFB revealed that intelligent monitoring of self-discharge can bring about up to 65% of energy savings during VRFB operation. The last challenge is associated with scale-up of VRFB to a kW-scale. In current state-of-the-art, there is no rationale to size the volume of electrolyte for a specific energy capacity. In this thesis, an empirical correlation is derived from dimensional analysis that can accurately predict the operational capacity or volume of electrolyte required for scaling-up a VRFB. The derived empirical correlation consisted of novel dimensionless numbers namely, n*umber of volume units* (NVU) and *theoretical capacity utilization* (TCU) along with known *Wagner Number* (Wa), and *reciprocal of Damköhler number* (RDa).

Keywords: Capacity-fade; Dimensional analysis; Electrode pre-treatment; Number of volume units; Scale-up; Theoretical capacity utilization; Vanadium redox flow battery.

सार

अक्षय ऊर्जा स्रोतों की आंतरायिक प्रकृति, एक विश्वसनीय और टिकाऊ ऊर्जा भंडारण प्रौद्योगिकी विकसित करने की आवश्यकता को निर्धारित करती है। विभिन्न उपलब्ध तकनीकों में, वैनेडियम रेडॉक्स फ्लो बैटरी (वीआरएफबी) बड़े पैमाने पर/स्थिर विद्युत ऊर्जा भंडारण अनुप्रयोग के लिए सबसे उपयुक्त तकनीकों में से एक है। वीआरएफबी में बड़ी संख्या में चार्ज-डिस्चार्ज चक्र (~ 20,000) से गुजरने की क्षमता है और साथ ही यह शक्ति और ऊर्जा को अलग कर सकता है। हालांकि, कुछ चुनौतियों के कारण वीआरएफबी का व्यापक व्यावसायीकरण अभी भी बाधित है। पहली चुनौती वीआरएफबी के लिए कुशल इलेक्ट्रोड सामग्री के विकास से जुड़ी है। वर्तमान में, ग्रेफाइट फेल्ट (जीएफ) वीआरएफबी के लिए व्यापक रूप से उपयोग की जाने वाली इलेक्ट्रोड सामग्री है। हालांकि, यह देखा गया है कि अनुपचारित जीएफ वीआरएफबी में अक्षम प्रदर्शन करते हैं और इसलिए इलेक्ट्रोड पूर्व उपचार आवश्यक है। वर्तमान में, उपलब्ध पूर्व-उपचार प्रक्रियाएं बड़े इलेक्ट्रोड के लिए निष्पादित करने के लिए या तो जटिल या गैर-व्यवहार्य हैं। इसलिए, यह थीसिस जीएफ के पूर्व-उपचार के लिए एक सामरिक प्रक्रिया प्रस्तुत करती है। पूर्व-उपचारित इलेक्ट्रोड में बड़े सतह क्षेत्र, अच्छी तरह से विकसित समान छिद्र संरचनाएं और प्रचुर मात्रा में ऑक्सीजन युक्त सतह कार्यात्मक समूह होते हैं। इस थीसिस में अपनाई गई सरल और सामरिक पूर्व-उपचार दृष्टिकोण जीएफ की चरम शक्ति घनत्व को 350 mW·cm-2 (अनुपचारित GF से 3 गुना वृद्धि) में सुधार करता है। बाद की चुनौतियां वीआरएफबी के संचालन के दौरान देखी गई तकनीकी बाधाओं से संबंधित हैं। यह ज्ञात है कि वीआरएफबी के संचालन के दौरान, वैनेडियम प्रजाति आयन एक्सचेंज मेम्ब्रेन (आईईएम) के पार जाती है। नतीजतन, कैपेसिटी फैड और सेल्फ-डिस्चार्ज की घटना सामने आती है। कैपेसिटी फैड से निपटने के लिए, यह थीसिस एक अद्वितीय इलेक्ट्रोलाइट मरम्मत बिंदु (ईआरपी) को संबोधित करती है जो वीआरएफबी के संचालन के दौरान इलेक्ट्रोलाइट मरम्मत के लिए सही समय की पहचान करने

के लिए एक तार्किक उपकरण है। इसके बाद, ईआरपी के आधार पर एक स्मार्ट इलेक्ट्रोलाइट स्वास्थ्य प्रबंधन प्रणाली तैयार की गई जो वीआरएफबी की स्थायित्व और दक्षता सुनिश्चित करने में सक्षम थी। कैपेसिटी फैड की तरह, सेल्फ-डिस्चार्ज प्रक्रिया भी आईईएम में वैनेडियम प्रजातियों के जटिल आंदोलन से निकटता से जुड़ी हुई है और प्रक्रिया के दौरान पर्याप्त मात्रा में ऊर्जा खो जाती है। इस चिंता को दूर करने के लिए, इस अध्ययन ने सावधानीपूर्वक डिजाइन किए गए प्रयोगों की सहायता से वीआरएफबी में स्व सेल्फ-डिस्चार्ज प्रक्रिया का अवलोकन किया। इसके अलावा, प्रयोगों से प्राप्त समझ को सामान्य बनाने के लिए एक गणितीय मॉडल विकसित किया गया था। विकसित गणितीय मॉडल ~ ± 10% की त्रुटि के भीतर वीआरएफबी के सेल्फ-डिस्चार्ज समय की सफलतापूर्वक भविष्यवाणी करता है और मॉडल की प्रभावकारिता के आधार पर किलोवाट स्केल वीआरएफबी पर एक केस-स्टडी से पता चला है कि सेल्फ-डिस्चार्ज की बुद्धिमान निगरानी ला सकती है वीआरएफबी संचालन के दौरान लगभग 65% ऊर्जा बचत। आखिरी चुनौती वीआरएफबी को किलोवाट-स्केल तक बढ़ाने से जुड़ी है। वर्तमान अत्याधुनिक में, किसी विशिष्ट ऊर्जा क्षमता के लिए इलेक्ट्रोलाइट के आयतन को आकार देने का कोई औचित्य नहीं है। इस थीसिस में, एक एम्पिरिकल सहसंबंध आयामी विश्लेषण से प्राप्त होता है जो वीआरएफबी के स्केल-उप के लिए आवश्यक इलेक्ट्रोलाइट की परिचालन क्षमता या मात्रा का सटीक अनुमान लगा सकता है। व्युत्पन्न अनुभवजन्य सहसंबंध में उपन्यास आयाम रहित संख्याएँ शामिल थीं, Number of volume units (NVU) और Theoretical capacity utilization (TCU) के साथ-साथ ज्ञात Wagner number (Wa), और Reciprocal of Damköhler number (RDA) के पारस्परिक।

मुख्य शब्द: कैपेसिटी फैड; आयामी विश्लेषण; इलेक्ट्रोड पूर्व उपचार; Number of volume units; स्केल अप; Theoretical capacity utilization; वैनेडियम रेडॉक्स फ्लो बैटरी.

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List of Abbreviations

ANOVA	Analysis of variance
BET	Brunauer Emmett Teller
BMT	Billion metric tones
CC	Constant current
CE	Columbic efficiency
Ce	Counter electrode
CEM	Cation exchange membrane
CNF	Carbon nano fiber
CNT	Carbon nano tube
CV	Cyclic voltammetry
EE	Energy efficiency
EIS	Electrochemical impedance spectroscopy
ERP	Electrolyte-repair-point
EDX	Energy dispersive X-ray spectroscopy
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
GF	Graphite felt
GNW	Graphene nano wall
GO	Graphene oxide
HER	Hydrogen evolution reaction
IEM	Ion-exchange membrane
KGF	Potassium hydroxide treated graphite felt
KTGF	Potassium hydroxide treated thermal graphite felt
LAB	Lead-acid battery
LCOE	Levelized cost of energy
LIB	Lithium-ion battery
MWCNT	Multi walled carbon nano tube
NVU	Number of volume units
OCV	Open circuit voltage
OEE	Overall energy efficiency

RDa	Reciprocal of Damköhler number
RE	Reference electrode
r-GO	Reduced graphene oxide
SoC	State of charge
TCU	Theoretical capacity utilization
TGA	Thermal gravimetric analysis
VE	Voltage efficiency
VRFB	Vanadium redox flow battery
Wa	Wagner number
WE	Working electrode

List of Nomenclatures

$\mathbf{A}$	Area of cation-exchange membrane (cm^2)
$\mathbf{C_0}$	Initial concentration of vanadium species (M)
$\mathbf{C_i}$	Concentration of *ith* vanadium specie at the outlet of VRFB cell (M)
$\mathbf{C^T_i}$	Concentration of *ith* vanadium specie in the electrolyte tank (M)
$\mathbf{E^o}$	Standard reduction potential (V)
$\mathbf{E_c}$	Energy required for charging ($W \cdot h$)
$\mathbf{ERP_{Max}}$	Electrolyte-repair-point
$\mathbf{E_{sd}}$	Energy lost during self-discharge ($W \cdot h$)
$\mathbf{F}$	Faraday's constant ($C \cdot mol^{-1}$)
$\mathbf{i}$	*ith* vanadium specie
$\mathbf{i_0}$	Exchange current (A)
$\mathbf{I_c}$	Charging current (A)
$\mathbf{I_d}$	Discharging current (A)
$\mathbf{j}$	Current density ($mA \cdot cm^{-2}$)
$\mathbf{k_0}$	Reaction rate constant ($m \cdot s^{-1}$)
$\mathbf{K_i}$	Mass-transfer coefficient of *ith* vanadium specie ($m \cdot s^{-1}$)
$\mathbf{K_w}$	Mass-transfer coefficient of water ($m \cdot s^{-1}$)
$\mathbf{M_w}$	Molecular weight of water ($g \cdot mol^{-1}$)
$\mathbf{n}$	Number of mole of electron transferred per mole of vanadium specie
$\mathbf{N_i}$	Overall flux of mass-transfer of *ith* vanadium specie ($mol \cdot cm^{-2}\ s^{-1}$)
NVU	Number of volume units
$\mathbf{P_p}$	Pump power requirement (W)
$\mathbf{q}$	Specific flow velocity ($cm \cdot s^{-1}$)
$\mathbf{Q}$	Electrolyte recirculation rate ($mL \cdot min^{-1}$)
$\mathbf{R_\Omega}$	Ohmic resistance (ohm)
RDa	Reciprocal of Damköhler number
$\mathbf{S_E}$	Geometric surface area of electrode (cm^2)
$\mathbf{SoC_{e+}}$	State of charge of positive electrolyte (%)
$\mathbf{SoC_{e-}}$	State of charge of negative electrolyte (%)
$\mathbf{SoC_i}$	Initial state of charge of VRFB cell (%)

SoC_f	Final state of charge of VRFB cell (%)
t_c	Charge time (h)
t_d	Discharge time (h)
t_{sd}	Self-discharge time (h)
TCU	Theoretical capacity utilization
ν	Scan rate ($mV\cdot s^{-1}$)
V_E	Geometric volume of electrode (cm^3)
V_T	Volume of electrolyte in tank (cm^3)
Wa	Wagner number
α_i	Stochiometric coefficient for formation or depletion of i^{th} vanadium specie due to instantaneous reaction
β_i	Stochiometric coefficient for depletion of i^{th} vanadium specie due to charge balance
Θ_i	Stochiometric coefficient for formation or depletion of *water* due to hydration sphere of vanadium species
δ_i	Stochiometric coefficient for formation or depletion of *water* due to instantaneous reaction of vanadium species
η_{act}	Activation overpotential (mV)
ρ_w	Density of water ($g\cdot cm^{-3}$)