DEVELOPMENT OF EFFICIENT AND COST-EFFECTIVE MEMBRANE FOR VANADIUM REDOX FLOW BATTERY

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DEVELOPMENT OF EFFICIENT AND COST-EFFECTIVE MEMBRANE FOR VANADIUM REDOX FLOW BATTERY

by

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Submitted

In fulfilment of the requirements of degree of Doctor Philosophy

to the

INDIAN INSTITUTE OF TECHNOLOGY DELHI

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Dedicated to

My Precious Ones

CERTIFICATE

This is to certify that the work contained in this thesis entitled, "**DEVELOPMENT OF EFFICIENT AND COST-EFFECTIVE MEMBRANE FOR VANADIUM REDOX FLOW BATTERY**" submitted by Mr. Utsav Dalal 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 COST-EFFECTIVE MEMBRANE FOR 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 interpretation put forth are based on my readings and understanding 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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(Utsav Dalal)

Abstract

Vanadium redox flow battery (VRFB) is emerging as an efficient and promising technology in terms of long-term cycling stability, constant power output, and outstanding safety for large scale applications. The crucial component of the VRFB system is the membrane/separator, which mitigate the cross mixing of electrolytes yet to provide ionic conductivity; but due to its high cost, it limits the commercialization of the VRFB system. The ion exchange membranes (IEMs) developed till date as an alternative to the commercial Nafion membrane could not be sufficient from the cost effectiveness due to their tedious and complex synthetic processes. A flawless membrane should have excellent proton exchange capability with minimum area resistance, low swelling ratio and sufficient water uptake along with restricted vanadium ion permeability. In this context, low-cost and negligible ionic resistance of the porous separators makes it a potential alternative to the high cost Nafion membranes. However, severe vanadium ion crossover through the micron size pores of the porous separator needs to be addressed. To tackle the same, three membrane/separators were explored and employed in the VRFB applications. The research work is focussed on the modification of the existing porous membranes/separators.

Effect of the loading of the Nafion solution is used as a filler in to the porous polyvinylidene fluoride (PVDF) membrane for reducing the crossover of the vanadium ion species. Scanning electron microscopy (SEM) confirmed the uniform penetration of the Nafion solution throughout the membrane. It is was found that water uptake, Nafion consumption (5 wt.%) and permeability of vanadium ions of PVDF-Nafion membrane are significantly smaller than the Nafion117 membrane. Vanadium permeability of PVDF-Nafion composite membrane reduced 18 times than that of the Nafion117 membrane. On flip side, the PVDF-Nafion composite membrane shows reduced ion conductivity. Therefore, in this work, a strategy is shown how

to tackle the additional overpotential due to reduced proton conductivity. Further, the effect of the thermal treatment on the porous network of the polyethylene (PE) separator is studied by exposing it to the high temperature within the range of 130℃ to 250℃. The vanadium ion permeability of the PE-Pristine separator (217×10^{-7} $cm^2\cdot min^{-1}$) reduced significantly to 9×10^{-7} $cm^2\cdot min^{-1}$ for the PE-170 separator owing to the decrease in the pore size. VRFB cell equipped with the PE-140 separator demonstrated optimum results in terms of better capacity retention, columbic efficiency (CE = 99%) and energy efficiency (EE = 70%). Further, the separator performance evaluated at a 3-cell VRFB stack with an effective area increased to 228 cm^2. Owing to the low EE, the PE separator was further modified wherein a cross-linked polyvinyl alcohol (PVA) layer is coated on to the PE separator to mitigate the vanadium ion crossover. PE-PVA separator showed better capacity retention with a capacity fade rate of 0.2% $Ah\cdot cycle^{-1}$ than the Nafion117 membrane (0.5% $Ah\cdot cycle^{-1}$). In-situ and ex-situ oxidative stability of the separator is explored in detail and a degradation mechanism of the cross-linked PVA membrane is proposed accordingly. The synthesized single side coated PE-PVA′ separator exhibits higher CE of 99% and comparable EE of 71% at a current density of 120 $mA\cdot cm^{-2}$ and demonstrated excellent lifetime durability tested up to 1600 charge-discharge cycles at 80$mA\cdot cm^{-2}$. In a parallel study, the performance of the recycled PFSA membrane is explored as a potential low-cost alternative to the Nafion117 membrane recycled from waste membrane. At last, the techno-economic assessment is done to justify the practicality of all the synthesized membranes for 1kW 1kWh VRFB system.

Keywords: Capacity retention; Membrane synthesis; PE separator; Self-discharge; Vanadium ion permeability; Vanadium redox flow battery.

सार

वेनेडियम रेडॉक्स फ्लो बैटरी (VRFB) तकनीक लंबी अवधि की साइकलिंग स्थिरता, निरंतर ऊर्जा उत्पादन, और बड़े पैमाने पर उपयोग के लिए उत्कृष्ट सुरक्षा के मामले में एक प्रभावी और आशाजनक तकनीक के रूप में उभर रही है। VRFB प्रणाली का सबसे महत्वपूर्ण घटक झिल्ली/विभाजक है, जो इलेक्ट्रोलाइट्स के इंटरमिक्सिंग को रोकता है और साथ ही आयनिक परिवहन प्रदान करता है; लेकिन इसकी उच्च लागत के कारण, यह VRFB प्रणाली के वाणिज्यीकरण को सीमित करता है। वाणिज्यिक नेफियन झिल्ली के विकल्प के रूप में विकसित आयन एक्सचेंज झिल्लियों (IEMs) जटिल और कठिन संश्लेषण प्रक्रियाओं के दृष्टिकोण से पर्याप्त नहीं हैं। एक बेहतरीन झिल्ली में उत्कृष्ट प्रोटॉन एक्सचेंज क्षमता होनी चाहिए, न्यूनतम क्षेत्र प्रतिरोध के साथ, कम सूजन अनुपात, पर्याप्त जल अधिग्रहण, और प्रतिबंधित वेनेडियम आयन पारगम्यता होनी चाहिए। इस संदर्भ में, छिद्रित विभाजक की कम लागत और नगण्य आयनिक प्रतिरोध इसे उच्च लागत वाली नेफियन झिल्लियों का विकल्प बनाता है। हालांकि, छिद्रित विभाजक के माइक्रोन आकार के छिद्रों से वेनेडियम आयन के अधिक क्रॉसओवर को संबोधित करने की आवश्यकता है। इसे हल करने के लिए, तीन प्रकार की झिल्लियों/ विभाजक का अध्ययन और VRFB अनुप्रयोगों में उपयोग किया गया। शोध कार्य का मुख्य उद्देश्य मौजूदा छिद्रित झिल्लियों/ विभाजक का संशोधन है।

वेनेडियम आयन के क्रॉसओवर को कम करने के लिए छिद्रित PVDF झिल्ली में फिलर के रूप में नेफियन सॉल्यूशन की मात्रा का प्रभाव देखा गया। स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोपी (SEM) ने झिल्ली के भीतर नेफियन सॉल्यूशन की समान रूप से प्रवेश की पुष्टि की। यह पाया गया कि PVDF-नेफियन झिल्ली का जल अधिग्रहण, नेफियन खपत (5 वज़न प्रतिशत), और वेनेडियम क्रॉसओवर नेफियन117 झिल्ली की तुलना में काफी कम है। PVDF-नेफियन कम्पोजिट झिल्ली की वेनेडियम पारगम्यता नेफियन117 झिल्ली की तुलना में 18 गुना कम हो गई। दूसरी ओर, PVDF-नेफियन कम्पोजिट झिल्ली में आयन परिवहन में

कमी दिखती है। इसलिए, इस कार्य में यह रणनीति प्रस्तुत की गई है कि कम प्रोटॉन परिवहन के कारण उत्पन्न अतिरिक्त ओवरपोटेंशियल से कैसे निपटा जाए। इसके अलावा, PE विभाजक के छिद्रित नेटवर्क पर थर्मल ट्रीटमेंट के प्रभाव का अध्ययन किया गया, जिसमें इसे 130°C से 250°C के उच्च तापमान से अवगत कराया। PE-प्रिस्टीन विभाजक (217×10^{-7} सेमी^{2}·मिन$^{-1}$) की वेनेडियम आयन पारगम्यता, छिद्र आकार में कमी के कारण, PE-170 विभाजक के लिए काफी घटकर 9×10^{-7} सेमी^{2}·मिन$^{-1}$ हो गई। PE-140 विभाजक से लैस वीआरएफबी सेल ने बेहतर क्षमता प्रतिधारण, CE (99%), और EE (70%) के संदर्भ में अनुकूल परिणाम प्रदर्शित किए। आगे, विभाजक के प्रदर्शन का मूल्यांकन 3-सेल वीआरएफबी स्टैक में किया गया, जिसमें प्रभावी क्षेत्रफल 228 सेमी^{2} तक बढ़ा दिया गया। कम ऊर्जा दक्षता (EE) को ध्यान में रखते हुए, PE विभाजक को और संशोधित किया गया, जिसमें PE विभाजक पर क्रॉस-लिंक्ड पॉलीविनाइल अल्कोहल (PVA) की परत कोट की गई, ताकि वेनेडियम आयन क्रॉसओवर को कम किया जा सके। PE-PVA' विभाजक ने बेहतर क्षमता प्रतिधारण दिखाया, जिसमें नेफियन117 झिल्ली (0.5% Ah·साइकल$^{-1}$) की तुलना में 0.2% Ah·साइकल$^{-1}$ की क्षमता क्षय दर पाई गई। विभाजक की इन-सिटू और एक्स-सिटू ऑक्सीडेटिव स्थिरता का विस्तार से अध्ययन किया गया और क्रॉस-लिंक्ड PVA झिल्ली का एक ह्रास तंत्र प्रस्तावित किया गया। संश्लेषित सिंगल-साइड कोटेड PE-PVA' विभाजक ने 120 mA·सेमी$^{-2}$ की धारा घनत्व पर 99% की उच्च CE और 71% की तुलनीय EE प्रदर्शित की, और 80 mA·सेमी$^{-2}$ पर 1600 चार्ज-डिस्चार्ज चक्रों तक परीक्षण में उत्कृष्ट जीवनकाल स्थायित्व दिखाया। अपशिष्ट झिल्ली से पुनर्नवीनीकृत PFSA झिल्ली के प्रदर्शन का मूल्यांकन नेफियन117 झिल्ली के लिए संभावित कम लागत वाले विकल्प के रूप में किया गया। अंततः, 1kW/1kWh VRFB प्रणाली के लिए सभी संश्लेषित झिल्लियों की व्यवहार्यता को सही ठहराने के लिए तकनीकी-आर्थिक मूल्यांकन किया गया।

मुख्य शब्द: क्षमता प्रतिधारण; झिल्ली संश्लेषण; PE विभाजक; स्व-प्रवृत्ति (सेल्फ-डिस्चार्ज); वैनाडियम आयन पारगम्यता; वेनेडियम रेडॉक्स फ्लो बैटरी ।

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List of Schemes

List of Abbreviations

EIA	Energy information administration
IEO	International energy outlook
BMT	Billion metric ton
EV	Electric vehicle
ICE	International combustion engine
LAB	Lead acid battery
LIB	Lithium-ion battery
VRFB	Vanadium redox flow battery
CEM	Cation exchange membrane
AEM	Anion exchange membrane
AIEM	Amphoteric ion exchange membrane
PBI	Polybenzimidazole
IEC	Ion exchange capacity
VE	Voltage efficiency
CE	Coulombic efficiency
EE	Energy efficiency
IEM	Ion exchange membrane
GO	Graphene oxide
MOF	Metal organic framework
MMM	Mixed matrix membrane
SPEEK	Sulfonated poly ether ether keton
SPAEK	Sulfonated poly aryl ether ketone
SPES	Sulfonated poly ether sulfone

NIPS	Non-solvent induced phase separation
VIPS	Vapor induced phase separation
EIPS	Evaporation induced phase separation
TIPS	Temperature induced phase separation
PAN	Poly acrylonitrile
TEOS	Tetraethyl orthosilicate
PVDF	Polyvinylidene difluoride
PES	Poly ether sulfone
PSSA	Poly styrene sulfonic acid
PVP	Polyvinyl pyrrolidone
PPY	Poly pyrrole
PI	Polyimide
PTFE	Poly tetra fluoroethylene
PE	Polyethylene
PVC	Polyvinyl chloride
PP	Polypropylene
TFC	Thin film composite
PVA	Polyvinyl alcohol
FESEM	Field emission scanning electron microscopy
EDX	Energy dispersive X-ray analysis
ATR-FTIR	Attenuated Total Reflectance-Fourier Transform Infrared
XRD	X-ray diffraction
TGA	Thermal gravimetric analysis
NMR	Nuclear Magnetic Resonance
BET	Brunauer-Emmett-Teller
WU	Water uptake

SR	Swelling ratio
ASR	Area specific resistance
IR	Infrared radiation
IRE	Internal reflection element
DI	De-ionized water
EIS	Electrochemical impedance spectroscopy
OCV	Open circuit voltage
GCD	Galvanostatic charge-discharge
GA	Glutaraldehyde
PFSA	Perfluoro sulfonic acid
DMF	Dimethyl formamide
SOC	State of charge
ESS	Energy storage system

List of Nomenclature

L	Thickness of the membrane (μm)
R	Area specific resistance ($\Omega \cdot cm^2$)
A	Effective area of membrane (cm^2)
φ	Porosity
ρ_{water}	Density of water ($g \cdot cm^{-3}$)
s	Conductivity ($mS \cdot cm^{-2}$)
P	Permeability ($cm^2 \cdot min^{-1}$)
V_{Cell}	Nominal voltage of single VRFB cell (V)
V_N	Nominal voltage of 1 kW VRFB stack (V)
j	Operational current density ($A \cdot m^{-2}$)
A'	Active electrode area in the VRFB stack (m^2)
C_{GF}	Cost of graphite felt ($\$ \cdot m^{-2}$)
C_V	Cost of vanadium precursor salt ($\$ \cdot kg^{-1}$)
C_{BP}	Cost of graphite bipolar plate ($\$ \cdot m^{-2}$)
C_{N117}	Cost of Nafion117 membrane ($\$ \cdot m^{-2}$)
C_{PE}	Cost of PE separator ($\$ \cdot m^{-2}$)
C_{PVDF}	Cost of PVDF membrane ($\$ \cdot m^{-2}$)
$\widehat{m}_V$	Mass of the vanadium precursor salt ($kg \cdot L^{-1}$)
$C_{E'}$	Cost of electrodes in the VRFB stack ($)
$C_{B'}$	Cost of bipolar plates in the VRFB stack ($)
$C_{M'}$	Cost of membrane in the VRFB stack ($)
C_{Stack}	Cost of VRFB stack ($)
$C_{Electrolyte}$	Cost of VRFB electrolyte in VRFB system ($)
C_{VRFB}	Cost of VRFB system ($)