SYNTHESIS AND CHARACTERIZATION OF ION EXCHANGE MEMBRANE FOR VANADIUM REDOX FLOW BATTERY

by

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in fulfillment of the requirements of the degree of Doctor of Philosophy

to the

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Dedicated to My Parents

CERTIFICATE

This is to certify that the thesis entitled **“SYNTHESIS AND CHARACTERIZATION OF ION EXCHANGE MEMBRANE FOR VANADIUM REDOX FLOW BATTERY”,** being submitted by Mr. MURALI MOHAN SEEPANA to the Indian Institute of Technology Delhi, for the award of the degree of Doctor of Philosophy in Chemical Engineering, is a record of bonafide research work carried out by him. MURALI MOHAN SEEPANA has worked under my guidance and supervision and has fulfilled the requirements for the submission of the thesis.

The results contained in this thesis have not been submitted in part or in full to any other university or institute for the award of any degree or diploma.

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MURALI MOHAN SEEPANA

Abstract

Renewable power generation systems are envisaged to increase contribution to total power generation and greater sensitivity of these systems' power generation capacity to environmental factors has resulted in a situation where at times the power generated is more than the demand and vice-versa. This has generated greater interest in large-scale storage of electric energy storage (EES) system as a valuable approach for improving the reliability and overall use of the entire power system generation, transmission, and distribution. Flow batteries with decoupled power and energy capacity provide attractive means of large scale EES. Vanadium redox-flow battery (VRB) has long cycle life, is the most developed and closest to commercialization of all flow batteries. Ion-exchange membrane (IEM) is a key component in VRB technology, as it dictates the performance and economic viability of the batteries. Commercial Nafion has disadvantages of high cost and low ion selectivity (i.e. high vanadium permeability) because of which alternative membranes are being sought. Finding and developing a suitable membrane to provide the right balance between performance and cost has now become a main focus of VRB research.

Inorganic materials have superior chemical stability and mechanical strength. Many of these materials are readily available at much cheaper cost than organic materials. Development of low cost IEM requires simple synthesis protocol with readily available ion exchangers and heat treatment/sintering at low temperature. Three membranes were successfully synthesized for VRB i.e. Polycarbonate (PC)-PWA, polytetrafluoroethylene (PTFE)-Zirconium phosphate (ZrP) and PTFE-PWA. Crystalline nature of ZrP and powder obtained from Si-PWA sol was

determined using XRD pattern. FTIR spectroscopy of the particles was done to show the presence of functional groups associated with ZrP and PWA respectively. Surface morphology of the membrane was studied using SEM and presence of crystalline phase in the membrane top-layer was shown by using thin film XRD. Mechanical strength, contact angle, water uptake, and oxidation stability of the synthesized membranes were found out. Ion exchange capacity and permeability of V(IV) ion were measured. Electrochemical impedance spectroscopy (EIS) was used to find the resistance of the membranes. VRB single cell tests with synthesized membranes were conducted on a potentiostat/galvanostat.

PC-PWA membrane showed water uptake of 28.9% and its burst pressure was 3.18kgcm^{-2}. Membranes' permeability to V(IV) ions measured at room temperature, was about half that of Nafion 115. Performance of VRB with PC-PWA membrane was poorer than one with Nafion 115 especially at higher current densities because of inferior columbic efficiency (CE). PC-PWA membrane gave reasonable efficiency in the VRB single cell but a lot more improvement is necessary before it can compete with already available commercial membrane. The lower CE values indicated greater cross-mixing of electrolytes which may be due high electrosmosis coefficient. Moreover, high swelling could have affected the ion selectivity of membranes and further lower its battery performance. Therefore PTFE-ZrP membrane with newer materials was synthesized and tested in VRB.

Vanadium ion permeability of the PTFE-ZrP membrane was three times less than the Nafion 115. EE of the VRB with PTFE-ZrP membrane was comparable to Nafion 115 for current densities up to 30mAcm^{-2}, but was lower at higher current density because of drop in the VE. PTFE-ZrP membrane could compete with Nafion115 in low current densities only.

Vanadium ion permeability of PTFE-PWA membrane was three times less than that of Nafion 115. Energy efficiency (EE) of VRB with Nafion115 was in the range of 70-85% whereas EE with PTFE-PWA membrane was 77-91%. EE of the VRB with PTFE-PWA membrane was better than Nafion for all current densities used in this work and it was also higher than that of PTFE-ZrP. Both CE and VE were higher than Nafion 115.

Contents

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