The Development and The Application of Porous Membranes Via Surface Modification For All-Vanadium Redox Flow Batteries

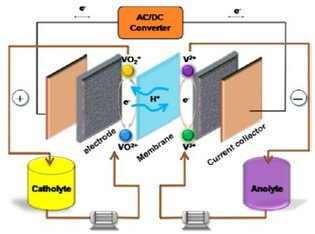
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Introduction

In this study, Amer-Sil FF60 porous membrane was chosen to be improved for an alternative membrane for VRFB applications. Besides, Nafion ®117, cation exchange membrane (CEM) and FAP 450, anion exchange membrane (AEM) was utilized to compare the results. The modification was applied with two different proportions by spraying technique. Unmodified and modified membranes were characterized in terms of VO^{2+} diffusion coefficient, ionic conductivity, water uptake and cell tests. After cell tests, Nafion stability test was applied for the control of Nafion's stability on the membrane surface.



A basic schematic of vanadium redox flow battery (VRFB) cell

Positive side reaction;

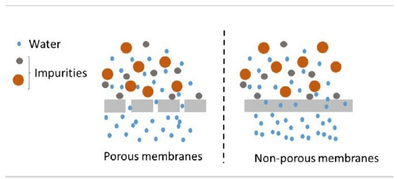
$VO^{2+} + H_2O + e^- \leftrightarrow VO_2^+ + 2H^+$ $E° = 1.004$ V

Negative side reaction;

$V^{3+} + e^- \leftrightarrow V^{2+}$ $E° = -0.255$ V

Overall reaction;

$VO^{2+} + H_2O + V^{3+} \leftrightarrow VO_2^+ + 2H^+ + V^{2+}$ $E° = 1.259$ V



The transport mechanism in porous (left) and non-porous (right) membrane

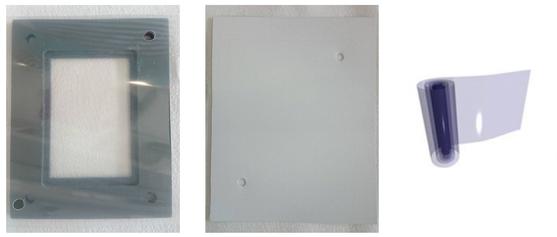
- The problem was mainly the crossover of vanadium electrolytes.
- The aim was to decrease the diffusion of redox active ions while maintaing the ionic conductivity as same as possible.



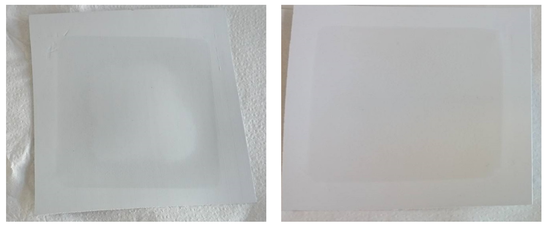
- It was planned to modify the membrane surface with Nafion® (5,7%,wt) dispersion via spraying technique such as (0,5:1) and (1:1) ratios.

Methods&Materials

The membranes were respectively below such as FAP 450 (AEM), Amer-Sil FF60 porous membrane Nafion 117(CEM), Amer-Sil FF60 /Nafion (5,7%, wt) (0,5:1) and Amer-Sil FF60 /Nafion (5,7%, wt) (1:1). Amer-Sil FF60 porous membrane's one face was coated with Nafion (5,7%, wt) dispersion with two different ratios. Ethanol was applied to carry the Nafion solution and its volume (ml) was not altered.

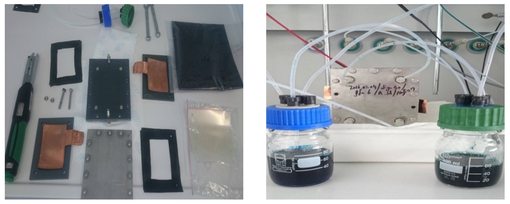


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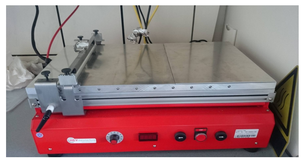


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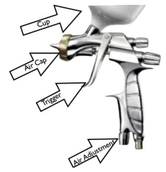
a: FAP 450, AEM Hydrophobic Backbone:Polyether ether ketone(PEEK) Thickness :0,01 cm
b: Amer-Sil FF60 porous membrane Hydrophobic Backbone:Polyvinylchloride(PVC) Hydrophilic Functional Group:Silica (Si) Thickness :0,064 cm
c: Nafion 117, CEM Hydrophobic Backbone: Polytetrafluoroethylene(PTFE) Hydrophilic Functional Group: Sulfonic acid (SO_3H) Thickness :0,01778 cm
d: Amer-Sil FF60/ Nafion® (5.7 %, wt) (0,5:1) membrane
e: Amer-Sil FF60/ Nafion® (5.7 %, wt) (1:1) membrane



Cell test components (left) and an operating cell with electrolyte vessels (right)



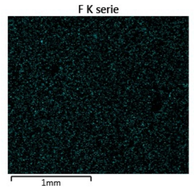
Dr.Blade for coating



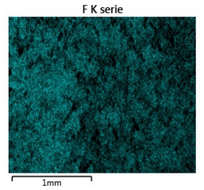
Spraying equipment for coating

Experimental Result

Energy Dispersive X-Ray Spectroscopy (EDX) was utilized for the analysis of which coating technique was more efficient.



Dr.Blade, Amer-Sil FF60 /Nafion , F distribution, Point 2, 20KV, 100X



Spraying, Amer-Sil FF60/Nafion , F distribution, Point 2, 20KV, 100X

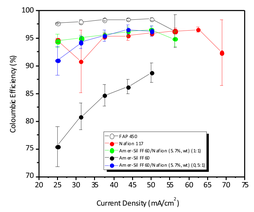
Table 1. Different modifying proportions of Amer-Sil FF60 porous membrane

Coating amount Nafion® (5,7 %, wt) (ml)	Coating amount Et-OH (ml)	Coating ratio
20	40	0,5:1
40	40	1:1

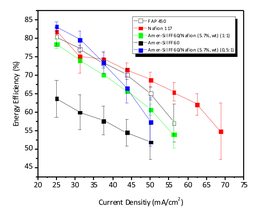
Table 2. The characterization values of all membranes

Membrane name	V^{4+}diffusion coefficients (cm^2 /min)	Ionic conductivity (S/cm)	Water uptake (%, wt)
FAP 450	$45x10^{-7}$	0,167	6,86
Nafion 117	$133,35x10^{-7}$	0,320	18,29
Amer-Sil FF60(porous membrane)	$499x10^{-7}$	0,345	105,32
Amer-Sil FF60/ Nafion® (5,7 %) (0,5:1)	$96x10^{-7}$	0,123	87,90
Amer-Sil FF60/ Nafion® (5,7 %) (1:1)	$19,2\ x10^{-7}$	0,073	74,89

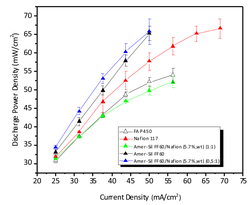
Cell Test Results



Coloumbic efficiencies(%) of all membranes

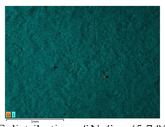


Energy efficiencies (%) of all membranes

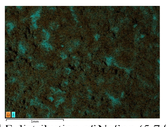


Discharge power densities (mW/cm^2) of all membranes

Nafion Stability Test



Cl and F distribution of Nafion (5.7 %,wt) dispersion on Amer-Sil FF60 porous membrane's surface before cell test, 100X, 20 KV



Cl and F distribution of Nafion (5.7 %,wt) dispersion on Amer-Sil FF60 porous membrane's surface after cell test, 100X, 20 KV

Conclusions

- With upon the addition of Nafion® (5,7%) dispersion, Amer-Sil FF60 porous membrane's relatively undesired and high permeability values could be decreased.
- It can be evaluated that the wettability and proton conductivity of the Amer-Sil FF60 decreased upon the addition of PTFE, Nafion's characteristic backbone.
- Considering the hydrophobic nature and different crystallinity of different polymers, PEEK(FAP 450) and PTFE controlled the membrane's swelling behavior. With upon their different crystallinity, the crytalline region of the membrane would extend and probably suppress their water absorption.
- As it could be seen from the Nafion stability results that Nafion dispersion could not stay on the membrane surface after the exposion of highly acidic medium.

Future Work

- It can be analysed of Nafion coating economically in detail.
- It can be experimented different modification methods in order to minimize the temperature effect due to the PVC's ,Amer-Sil FF60's backbone, glass temperature around 60° C.
- It can be characterized in terms of mechanical test before/ after modification, pore size and tortousity alteration after modification [4].

References

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Acknowledgements

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