DEVELOPMENT OF DISULFONATED POLY(ARYLENE ETHER SULFONE) COPOLYMER MEMBRANES FOR Li^+ FLOW BATTERIES

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INTRODUCTION

Redox Flow Batteries (RFB), being representatives of flow battery family, are known for their long-lasting life services, simple manufacturing, low cost and safety. They operate as rechargeable batteries and are highly suitable for long-term energy storage. Li^+ flow batteries, based on the principle of using lightweight Li^+ as their charge carrier, combine the advantage of high energy density of Li^+ ions with the rechargeability and flexibility of flow batteries. These electrochemical cells that consist of two solutions providing the chemical energy are separated by polymeric ion exchange membranes. These membranes prevent the crossover of the charged molecules. The selection of the suitable membrane for Li RFBs is a crucial parameter as it is directly related to the ion exchange capacity of membranes and performance of the systems. In this study, for the very first time, disulfonated poly (arylene ether sulfone) (BPSH) copolymer membranes have been introduced into Li RFB systems as alternative to widely used Nafion™. BPSH membranes, primarily being synthesized in their salt (Na^+) forms, have been converted into Li^+ form by sequential protonation and lithiation steps. Chemical and structural properties of copolymer membranes have been studied via various characterization methods such as FTIR, RAMAN, TGA, AFM. Moreover, basic electrochemical membrane properties such as %water uptake capacity, H^+ and Li^+ conductivities have been analyzed.

MATERIALS AND METHODS

- **Membrane Casting:** Salt form of BPSH copolymers have been dissolved in DMAC and casted under IR lamp overnight. (Fig 1a.)
- **Acid Treatment:** Prepared membrane have been acidifed by being boiled in 0.5M H_2SO_4 for 2hrs followed by boiling in deionized H_2O for 2 more hrs (Fig 1b.)
- **Lithiation:** H^+ form membranes have been kept in 1M $LiClO_4$ solution at different time periods and their Li^+ conductivities have been measured
- **Electrochemical Characterizations:** H^+ and Li^+ conductivities of BPSH membranes have been evaluated via Bekktech Conductivity cell equipped with Solartron 1260&1287A Sourcemeter. Deionized water have been used for H^+ and various [$LiClO_4$] have been used for Li^+ conductivity measurements

RESULTS & DISCUSSION

The obtained results have shown that a correlation exists between the conductivity of lithiated membranes and molarity of conducting solution. The highest lithium conductivity was measured as 39.07 $S.cm^{-1}$ at 1M $LiClO_4$ solution. Moreover, the degree of the chemical interaction of Li^+ ions with the sulfonate functional groups has been demonstrated by several methods such as FTIR and RAMAN studies. The FTIR peak shift at 1140 cm^{-1} and Raman shifts at 1155 cm^{-1} correspond to the interaction taking place between Li^+ ions and the membrane (Fig 2 a&b). The %water uptake capacity strongly depending on the block lengths of hydrophilic and hydrophobic domains have been observed to be highest for Li^+ form membrane (Fig. 2c). The influence of lithiation period and the effect of [$LiClO_4$] solution to the conductivity of membrane have also been investigated and the results have been summarized in Table 1 and Fig 2d. AFM studies have revealed that hydrophilic and hydrophobic domains have been well defined for acid and salt (Li^+ and Na^+) form of the membranes. Moreover, a significant increase in hydrophilic regions have been observed in the protonated membrane form.

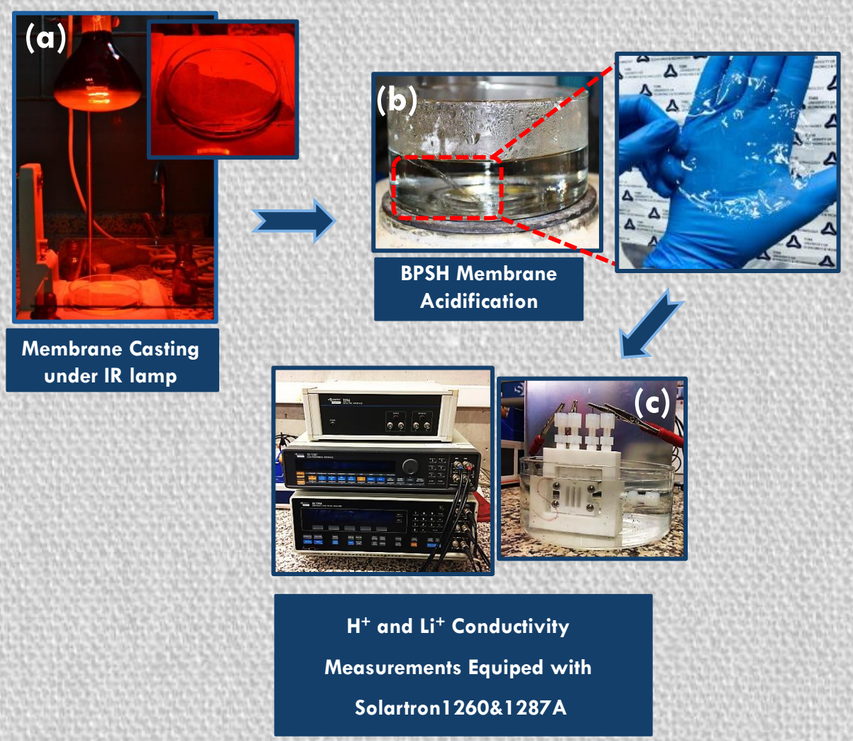


Figure 1. Experimental set-up of **(a)** membrane casting **(b)** acidification and **(c)** electrochemical characterizations

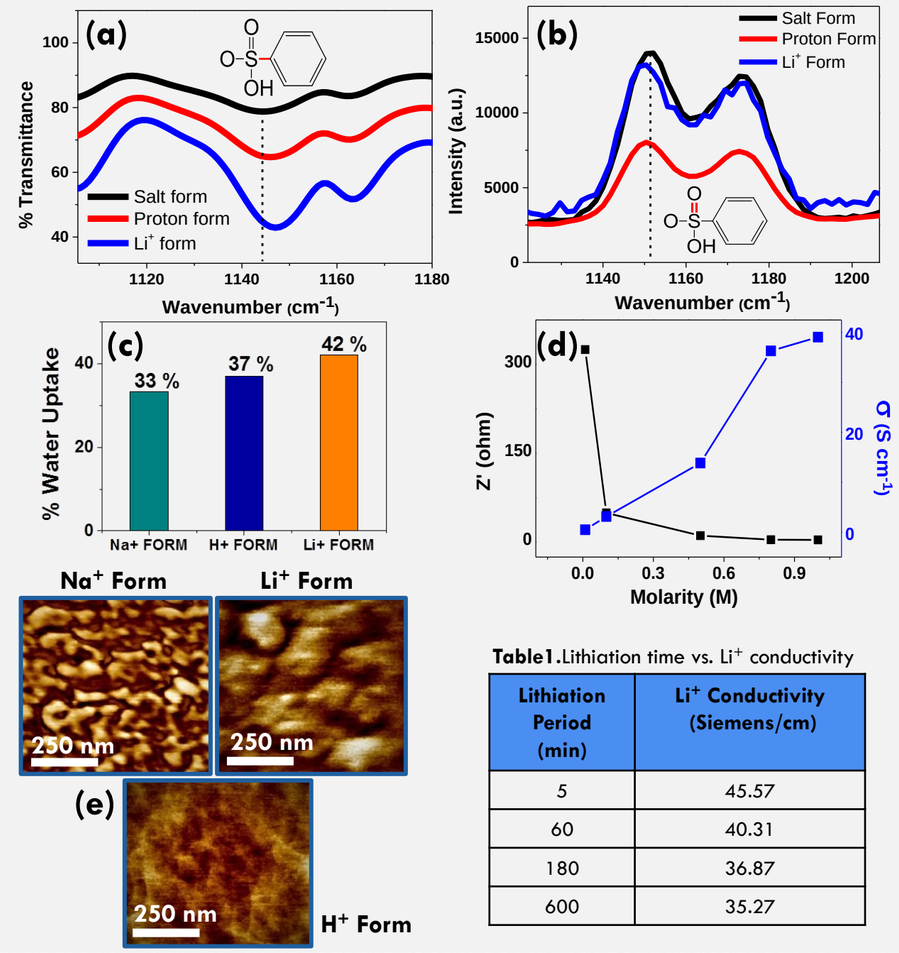


Table1. Lithiation time vs. Li^+ conductivity

Lithiation Period (min)	Li^+ Conductivity (Siemens/cm)
5	45.57
60	40.31
180	36.87
600	35.27

Figure 2. Structural characterization of BPSH via **(a)** FTIR and **(b)** Raman Analysis, **(c)** % water uptake values of salt and acid forms of membranes, **(d)** conductivity-molarity correlation for BPSH membranes, **(e)** AFM images of salt and acid forms of BPSH

CONCLUSIONS

The degree of lithiation at 60 minutes have been selected as the most favorable one for Li RFB applications. Successfully lithiated membranes are found to be highly suitable for RFB systems .

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REFERENCES

[1] Semiz L, Sankir N D, Sankir M (2014) Directly Copolymerized Disulfonated Poly(arylene ether sulfone) Membranes for Vanadium Redox Flow Batteries. International Journal of Electrochemical Science 9: 3060-3067

[2] Huang Q, Yang J, Ng C B, Jia C, Wang Q (2016) A redox flow lithium battery based on the redox targeting reactions between LiFePO4 and iodide. Energy & Environmental Science 9: 917-921