

Synthesis and Proton Conductivity of Nafion with Addition of CsHSO₄

Bruno R. Matos^{1*}, Leticia P. R. Moraes¹, Elisabete I. Santiago¹ and Fabio C. Fonseca¹

¹Centro de Células a Combustível e Hidrogênio/Instituto de Pesquisas Energéticas e Nucleares, Brazil, brmatos@usp.br

INTRODUCTION

Anhydrous solid electrolyte membranes with high proton conductivity at intermediate temperatures (150–250 °C T-range) are considered key materials for obtaining high power density output in polymer electrolyte fuel cells (PEFC), such as proton exchange membrane fuel cells (PEMFC), direct alcohol fuel cells (DAFC) and direct methane fuel cells (DMEFC) [1,2]. High proton conductivity ($\sim 10^{-2} \text{ Scm}^{-1}$) has been observed in superprotonic conductor solid acids (CSPs) such as CsHSO₄ at $T > 140^\circ\text{C}$. The use of such materials in PEFCs has simplified the water management and provided high current densities at an intermediate temperature range. However, the CSP thin films are fragile, water soluble, and the fabrication of low thickness (low ohmic resistance) films is a hard task [2]. On the other hand, polymer electrolytes such as Nafion are flexible and can be obtained in a broad range of thicknesses. However, at anhydrous conditions, these membranes are electrical insulators. In this context, the fabrication of composite membranes based on the addition of CsHSO₄ into Nafion matrix at concentrations above the percolation threshold of the inorganic phase can substantially improve the proton conductivity at intermediate temperatures ($T > 140^\circ\text{C}$). Herein, we show that the addition of CsHSO₄ into Nafion at high loadings, a pronounced increase of the proton conductivity is obtained.

EXPERIMENTAL/THEORETICAL STUDY

Commercial Nafion 115 membranes were cleaned and activated with standard washing protocols by immersing the membranes in H₂O₂ (3vol%) and H₂SO₄ (1molL⁻¹) with intermediate washing steps with deionized water until neutral pH is reached. The composite membranes were prepared by the *in situ* incorporation of CsHSO₄ by the evaporation/precipitation method. In order to incorporate high loading of the CsHSO₄ into Nafion, these membranes were previously heat-treated in autoclave at 140 °C for 2h under water to promote an irreversible swelling of the Nafion nanopores. An alternative method to increase the membrane swelling is the immersion of Nafion in dimethylsulfoxide (DMSO) solution. The Nafion+CsHSO₄ (NCSP) composite preparation consists in immersing the Nafion membranes in a CsHSO₄/DMSO/H₂O solution for 1h at room temperature and at 160 °C for 6h for the complete evaporation of the solvents. The prepared membranes were characterized by infrared spectroscopy (FTIR), X-ray diffraction (DRX), small angle X-ray scattering (SAXS) and proton conductivity under N₂ flow.

RESULTS AND DISCUSSION

Figure 1 shows the anhydrous proton conductivity of NCSP composites possessing different volume fraction of the second phase.

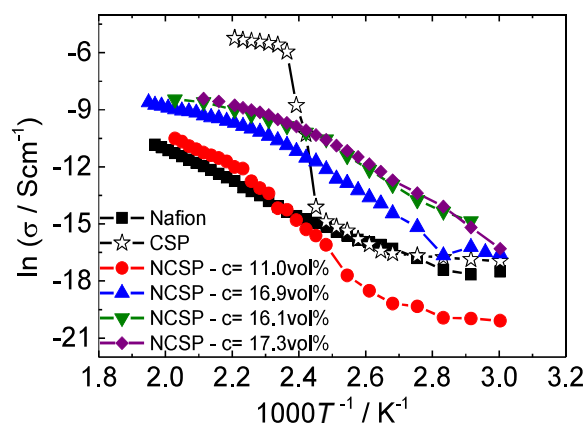


Fig. 1 Arrhenius plots for Nafion and NCSP composites under N₂ flow at different volume fractions of the inorganic phase.

At low volume fraction, the proton conductivity of the NCSP is similar to the one observed for Nafion. However, at higher concentrations, $c \geq 16.1 \text{ vol}\%$, a pronounced increase of the proton conductivity is observed that can be attributed to the higher connectivity of the inorganic phase into the insulating Nafion matrix.

CONCLUSION

Highly-stable proton conducting membranes based on Nafion+CsHSO₄ were obtained. The addition of CsHSO₄ improves significantly the proton conductivity of Nafion at anhydrous condition. The resulting proton conductivity is a result of the combination of the transport and physical properties of the host matrix and the added inorganic filler.

REFERENCES

1. M. Joglekar, V. Nguyen, S. Pylypenko, C. Ngo, Q. Li, M. E. O'Reilly, T. S. Gray, W. A. Hubbard, T. B. Gunnoe, A. M. Herring, B. G. Trewyn, J. Am. Chem. Soc. 138, 116 (2016).
2. S. M. Haile, D. A. Boysen, C. R. I. Chisholm, R. B. Merle, Nature 410, 910 (2001).

ACKNOWLEDGMENTS

Thanks are due to the Brazilian funding agencies (CAPES, CNPQ, FAPESP-2013/50151-5).