

IVo11-001

Electrostatic interactions of Ionomer Films as Probed by Variable Temperature Synchrotron Infrared Spectroscopy

Da Silva, J.S.(1); Matos, B.R.(1); Schade, U.(2); Puskar, L.(2); Fonseca, F.C.(3); Instituto de Pesquisas Energéticas e Nucleares(1); Instituto de Pesquisas Energéticas e Nucleares(2); Helmholtz-Zentrum Berlin(3); Helmholtz-Zentrum Berlin(4); IPEN-CNEN/SP(5);

The state of the art polymer electrolyte of Proton Exchange Membrane Fuel Cells (PEM), Nafion®, has poor mechanical and electrical properties at $T > 100\text{ }^{\circ}\text{C}$. Specifically, long-term operation leads to irreversible performance losses that are related to an irreversible modification of the ionomer morphology above the temperature of alpha-transition ($T_{\alpha} \sim 110\text{ }^{\circ}\text{C}$). Previous characterizations showed that the alpha-transition is dependent on the different states of covalent and ionic interactions among sulfonic acid groups, such as: ionic repulsions among RSO_3^- , dipolar attractions among RSO_3H dipoles, hydrogen bonding of sulfonic groups with bulk and coordinated water molecules. The identification of both the functional groups interactions in the MIR bands and the “ion-hopping bands” in the FIR bands for annealed Nafion samples can give new insights into the role played by the ionic interactions on the alpha of ionomer membranes. Such approach for understanding the relationship between the dynamics of alpha-relaxation and Nafion morphology is missing in the literature, possibly due to the incipient number of FIR studies of Nafion. The central objective of this work is to advance the understanding of the chemical features involved during the alpha-transition of in situ annealed Nafion membranes with the high-resolution mid (MIR) and far (FIR) infrared spectroscopy using the IRIS beamline of BESSY II synchrotron light source. Herein, the effect of short-term annealing of Nafion at RH $\sim 0\%$ and selected temperatures below and above the alpha-transition is presented. The comparison between SAXS and FTIR data of Nafion membranes annealed in situ revealed that the alpha-transition is due to the long range motion of the ionomer chains via weakening of electrostatic interactions of the ionomer functional groups.