

Abstract

This PhD thesis investigates and optimizes next-generation short-side-chain (SSC) perfluorosulfonic acid ionomers, commercially known as Aquivion®, for application in proton exchange membrane fuel cells (PEMFCs). The research was carried out in collaboration with Syensqo SA and focuses on understanding how ionomer chemistry, membrane type, interfacial architecture, and operating conditions jointly affect electrochemical performance, durability, and scalability—key aspects for enabling high-efficiency and long-lasting fuel cells in sustainable energy and mobility. The work follows a multiscale experimental approach, integrating half-cell screening, single-cell validation, and accelerated stress testing (AST) with complementary *ex situ* characterization. In the first phase, the catalyst–ionomer interaction was studied through optimization of catalyst ink formulations using the gas diffusion electrode (GDE) half-cell configuration. The optimal ionomer-to-carbon (I/C) ratio of 0.6 was identified as a universal condition for both Nafion® and Aquivion®, ensuring an effective balance between proton conductivity and oxygen transport. Morphological analysis revealed that Aquivion®—especially low equivalent weight (EW) grades—forms more continuous and homogeneous ionomer–catalyst networks, improving ionic connectivity but increasing flooding susceptibility at high current densities due to reduced porosity. In the second phase, the optimized GDEs were integrated into membrane–electrode assemblies (MEAs) and tested in single-cell configuration at Syensqo’s R&D facilities. Single-cell validation confirmed the predictive capability of half-cell screening. While Nafion®-based MEAs maintained slightly better performance at high current densities due to higher porosity and better water removal, Aquivion®-based systems exhibited superior proton transport and higher activity in the kinetic region. Durability was then investigated through carbon corrosion ASTs in both single-cell and half-cell configurations. Despite exhibiting stronger carbon oxidation and larger electrochemical surface area (ECSA) loss, Aquivion®-based MEAs showed better performance retention after stress, attributed to their denser and more cohesive CL microstructure, which provides mechanical robustness and maintains protonic continuity. This behavior highlights the critical balance between ionomer chemistry, morphology, and electrochemical degradation pathways. In the final phase, the study extended to hybrid and fully Aquivion®-based MEAs featuring an ionomer overlayer at the CL–membrane interface. This additional layer significantly improved interfacial contact, reduced ohmic and charge-transfer resistances, and enhanced water management. Under low-humidity operation, the overlayer proved especially beneficial, ensuring better hydration and stable performance. Fully Aquivion®-based systems achieved the highest current densities and lowest resistive losses. Under fully humidified conditions at elevated temperature, a slight performance decline was observed, explained by the thermodynamic reduction in oxygen partial pressure, which limits O₂ availability at high current densities. Nafion®-based MEAs, operating at lower current densities, were less affected by this phenomenon. Overall, this thesis establishes a comprehensive framework linking ionomer structure, catalyst–ionomer interactions, and interfacial engineering to PEMFC performance and durability. It demonstrates that SSC-Aquivion® ionomers, combined with appropriate interfacial design, can match or even surpass traditional Nafion® systems, particularly under challenging low-humidity conditions. These findings advance the understanding of fundamental structure–property relationships in ionomer-based electrodes and contribute to the development of durable, high-efficiency, and scalable PEMFCs, supporting the global transition toward sustainable energy and decarbonized transportation.