

SUMMARY

This thesis focuses on the development and electrochemical evaluation of advanced iron-nitrogen-carbon (FeNC) catalysts for the oxygen reduction reaction (ORR) in proton exchange membrane fuel cells (PEMFCs). The commercialization of PEMFCs is hindered by the high cost and limited availability of platinum-based catalysts. FeNC catalysts offer a promising alternative, as they are made from abundant, low-cost elements while maintaining high catalytic activity. The research presented here systematically explores the synthesis, characterization, electrochemical behavior, and fuel cell performance of FeNC catalysts.

The synthesis of FeNC catalysts was carried out using a hard-template method, employing mesoporous silica templates such as SBA-15, KIT-6, and a dual-template approach combining both. Starting from these templates, three different catalysts were achieved: FeNC^{SBA-15}, FeNC^{KIT-6}, and FeNC^{SBA-15/KIT-6}. This approach allows the tailoring of catalyst morphology and the enhancement of the distribution of active sites. The mesoporous structure is crucial for maximizing the surface area and ensuring efficient mass transport, which significantly impacts the catalytic performance. Then, several template removal techniques have been investigated, including acid leaching with hydrofluoric acid (FeNC^{HF}), basic leaching with sodium hydroxide followed by hydrochloric acid treatment (FeNC^{NaOH+HCl}), and an acid-free Teflon-assisted method (FeNC^{PTFE}).

The catalytic properties of the FeNC catalysts were evaluated through extensive physicochemical characterization, including X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and nitrogen sorption analysis, which provided insights into the surface composition, porosity, and morphology of the catalysts.

The FeNC catalysts were first assessed using the rotating disk electrode (RDE) technique to investigate their ORR activity. Various parameters such as ionomer-to-carbon ratio and catalyst loading were optimized. The FeNC catalysts exhibited promising ORR performance, with the FeNC^{NaOH+HCl} catalyst showing an onset potential of 0.93 V_{RHE} and a half-wave potential of 0.71 V_{RHE} in alkaline media, approaching the performance of platinum-based catalysts. The electrocatalytic activity was further confirmed by Koutecky-Levich (KL) analysis and rotating ring disk electrode (RRDE) measurements, which revealed a near four-electron transfer pathway, indicating high ORR efficiency with minimal hydrogen peroxide formation.

Subsequent electrochemical testing was performed using the gas diffusion electrode (GDE) technique, which better simulates the real conditions of a PEMFC. The GDE setup incorporates the triple-phase boundary, where the catalyst, electrolyte, and gas phases interact, providing a more accurate assessment of catalyst performance under realistic fuel cell conditions. This setup confirmed the high activity of the FeNC catalysts, especially in comparison to the commercial platinum catalyst.

In fuel cell testing, three different membrane electrode assembly (MEA) strategies were explored: a standard assembly, a hot-pressed MEA, and an MEA with a Nafion overlayer deposited onto the cathode before hot-pressing. The Nafion overlayer improved proton

conductivity and reduced activation losses, resulting in a higher peak power density of 350 mW/cm² for the FeNC^{NaOH+HCl} catalyst at a current density of 1 A/cm². The performance of the MEAs was also evaluated at different relative humidities (RH) of 75%, 100%, and 120%. The best performance was observed at 100% RH, where proton conductivity was optimized without flooding effects. The performance decreased at higher RH due to flooding, highlighting the importance of water management in PEMFC operations.

To complement the experimental findings, a numerical model was developed using COMSOL Multiphysics to simulate PEMFC performance. The model accounted for key factors such as mass transport, gas diffusion, and electrochemical reactions. Simulations were conducted at varying RH levels to understand their impact on fuel cell performance. The model successfully predicted the experimental polarization curves, providing a deeper understanding of how relative humidity affects proton conductivity and fuel cell efficiency. Future improvements to the model could include the incorporation of additional factors such as temperature, catalyst degradation, and more detailed water management processes.

The findings of this research demonstrate that FeNC catalysts can serve as a viable, cost-effective alternative to platinum for PEMFCs. The FeNC catalysts exhibit excellent ORR performance, high stability, and good fuel cell efficiency, all while being significantly less expensive than platinum-based catalysts. The combination of experimental results and numerical modeling offers a comprehensive understanding of the factors influencing FeNC catalyst performance and provides valuable insights for future optimization.

This work paves the way for further developments in FeNC catalysts, focusing on enhancing their stability, optimizing the ionomer-catalyst interaction, and developing advanced MEA architectures. Future research could explore different synthesis methods to further improve catalyst performance, incorporate low platinum loadings for additional enhancements, and investigate the potential of alternative ionomers or membrane materials in combination with FeNC catalysts. This study contributes significantly to the ongoing effort to reduce the cost of fuel cell systems while improving their performance, bringing us closer to a more sustainable energy future.