Functionalizing monolayer graphene as a proton-selective membrane for direct methanol fuel cells

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Chapter 6

Conclusions and Outlooks: Graphene, fuel cells and perspectives.

This thesis focused on the exploration of monolayer graphene as a membrane in direct methanol fuel cell (DMFC) applications, with improvements achieved through plasma exposure or damage-free chemical functionalization. The advancements in low-dimensional materials (LDMs) have unveiled a new era where artificial membranes can regulate ion transport with atomic precision (**Chapter 1**). In the context of DMFCs, a large-scale membrane that allows selective proton transport is essential for bridging the two half-reactions. Therefore, a DMFC is a very restrictive device to challenge the membranes. Achieving high proton selectivity while keeping conductivity is challenging for state-of-the-art proton-selective membranes using LDMs. Traditional LDMs are typically made in the form of nanoflakes or tubes, which, when assembled into a membrane with a polymeric matrix, introduce extra resistance and hinder energy efficiency. To address this issue, the thickness of the membrane needs to be minimized, ideally reaching atomic thinness. Graphene, which can be fabricated at centimeter-scale using chemical vapor deposition (CVD), was chosen as a potential solution. However, while graphene exhibits excellent proton selectivity, its perfect monolayer crystal has insufficient proton conductance for DMFCs. Thus, the focus shifted to studying defect generation in graphene to tune its proton conductance and overall performance.

Plasma exposure emerged as a straightforward method to etch carbon in the graphene lattice, leading to the formation of vacancy defects (**Chapter 2**). By investigating the effects of different plasma sources, such as nitrogen and argon, as well as varying exposure conditions such as time and power, the changes in graphene properties were elucidated. Interestingly, this approach enabled the isolation of vacancy defects and dopants, which may add to long-standing debates in the field of oxygen reduction reaction (ORR) catalysts based on carbon materials. It was discovered that vacancy defects enhance ORR activity, regardless of the presence of nitrogen dopants, and reduce the overpotential. Nitrogen dopants, under negative voltages, also improve the ORR current. However, in the absence of vacancy defects, nitrogen dopants increase the overpotential. Furthermore, nitrogen dopants enhance the selectivity of the $2e^-$ pathway, resulting in an increased production of peroxide. These findings not only contribute to a better control of defect generation in graphene but also offer valuable insights into carbon-based ORR catalysts.

To fabricate a centimeter-scale graphene membrane with minimal ionomer content, a method involving a porous support and a small amount of ionomer for protection was developed (**Chapter 3**). The variations observed in proton/methanol selectivity and proton conductivity among different graphene samples highlighted the importance of controlling inherent defects to achieve optimal membrane performance. Intentional defect engineering, to increase proton conductivity while maintaining proton selectivity, becomes crucial to match or surpass the performance of polymer membranes.

The quality of graphene and the influence of introduced defects on DMFC performance were further investigated using two typical graphene samples with and without multilayer patches (**Chapter 4**). Single-crystalline graphene (SCG) exhibited higher proton conductance at low temperatures compared to polycrystalline graphene (PCG). However, SCG showed higher methanol leakage at elevated temperatures, indicating lower tolerance to operating conditions. Multilayer patches on PCG were found to stabilize the membrane, contributing to improved temperature tolerance. Plasma treatment introducing defects increased the conductance of both SCG and PCG. However, defective SCG membranes experienced higher methanol crossover, while defective PCG membranes showed lower methanol permeation and higher power output. These findings highlight the significant role of multilayer patches in stabilizing the graphene membrane, enhancing temperature tolerance, and providing higher proton/methanol selectivity. The presence of multilayer patches from controlled CVD growth in DMFC allowed for higher robustness and proton selectivity.

Although plasma-induced defects in graphene did not surpass the proton conductance of current polymeric proton exchange membranes, an alternative approach involving the treatment of graphene with sulfophenyl radicals was explored (**Chapter 5**). This method, proposed by Xue Liu, aimed initially to functionalize graphene as a two-dimensional version of Nafion, a typical polymer proton exchange ionomer. The results showed highly selective proton conductivity (~50 S cm^{-2} at room temperature) and enabled application in DMFCs, achieving a power density more than twice that of Nafion counterparts when normalized to the electrode area (127 mW cm^{-2} at 60 °C). These findings call for further understanding of the reactions and mechanisms responsible for such high conductance values in functionalized graphene. Theoretical insights into proton transport through sp^3-distorted graphene, tuning of proton tunneling barriers, and the importance of functional distortion geometry and polarity are required. Increasing the sp^3 density could potentially enhance proton conductance through functionalized graphene. Polarizing a 2D membrane may also play a crucial role in controlling ion translocation-transport, including more complex two-dimensional polymer architectures.

Looking ahead, the development of membranes made of LDMs holds promising prospects. While graphene and graphene-like carbon films have demonstrated their potential in growing to centimeter scale, there is a need to explore new 2D films, such as recently reported amorphous carbon films. Designing building blocks for these films would allow precise control over membrane properties from the initial stages. Additionally, the advancements in 2D polymers, involving the conjugation of molecules into larger films, present an exciting avenue for research.

Understanding proton transport in ultra-confined spaces compared to their bare size remains a challenge. Although observation and characterization approaches are currently lacking, computational results can guide future directions. Proton transport likely occurs through subnanometer barriers via tunneling, and the charge effect and sp^3 distortion may facilitate transport. Further investigations are required to gain a comprehensive understanding of proton transport mechanisms.

The trade-off between selectivity and conductivity, which has impeded the development of proton exchange membranes, has been overcome through monolayer graphene, making it applicable in large-scale devices such as DMFCs. This work has the potential to solve many challenges faced by devices requiring proton exchange membranes, extending beyond fuel cells. The vision of widely applying liquid fuel cells instead of relying on numerous batteries under car seats is a possibility worth pursuing. Furthermore, the beauty of LDMs lies in their precise structural properties, which should never be compromised merely for incremental improvements in conventional technologies.