学 位 論 文 の 要 旨

Modification of graphene oxide membrane and its applications in proton exchange membrane fuel cells

(酸化グラフェン膜の修飾とそのプロトン交換膜燃料電池への応用)

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Nafion (Dupont) with the excellent chemical stability and proton transport ability is the most widely used proton exchange membrane (PEM) for fuel cells. However, the large-scale application of Nafion has been limited by its high cost (1400-2200 USD m^{-2}). Graphene oxide (GO) membrane can be modified to have a proton conductivity and is expected to be an alternative membrane with lower price, due to the cheap and abundant raw material graphite. However, the proton conductivities of the current GO membranes are still much lower than that of the Nafion membrane. Therefore, improving the proton conductivity of GO membrane is a very important research subject. At the same time, for the fuel cell applications, GO membrane needs to have adequate mechanical strength. In this thesis, a method for preparing a GO membrane that has high and stable proton conductivity while suppressing its swelling in water are investigated, with the aim of applying it to the electrolyte membrane of fuel cells.

In Chapter 1, the background of GO membrane for fuel cells is introduced, and the research subjects and the chapter structure of this thesis are described. The research challenges of GO membranes for fuel cells are their low proton conductivity and high swelling ratio. The ozone (O_3) treatment is a simple and effective method to improve the oxygen functional groups and proton conductivities of the GO membrane. However, the previous studies have not explored optimal treatment conditions to improve the fuel cell power output. Crosslinking between GO nanosheets with a crosslinking agent has been used to reduce the swelling. However, the previous agent with amin group widely used reduce the oxygen content and reduce the conductivity. Crosslinking with other agent that can further improves the conductivity and reduces its swelling is necessary.

In Chapter 2, to obtain the higher proton conductivity, GO solution was treated by bubbling ozone gas to add the oxygen-containing functional groups on GO surface, and the effect of different treatment time (0 min, 60 min, 120 min and 140 min) was investigated. As increasing the treatment time, the oxygen content (O/C ratio) and the carbon defect, obtained by XPS analysis, increased, and the conductivities, both of in-plane and through-plane, increased. This suggested that the number of proton transfer sites increased and the proton conduction path shortened by the treatment. However, with the treatment for 140 min, the failure of the membrane fabrication occurred due to excessive oxidation including size reduction of GO molecule. At the optimum treatment time for 120 min, the through-plane conductivity was improved from 0.47 mS cm^{-1} to

10.3 mS cm^{-1}, and the fuel cell power output was also improved from 21.9 mW cm^{-2} to 196 mW cm^{-2}. However, these membranes remained the problem of severe swelling and dissolution in water.

In Chapter 3, to reduce the swelling in water and further improve the conductivity, crosslinking of the GO nanosheets with oxygen-containing functional groups was proposed and studied. As the crosslinkers with the oxygen functional groups, glyoxal (GLX) with -CHO and oxalic acid (OXA) with -COOH groups, were applied for the ozone-treated GO (GOL). The membranes modified with these crosslinkers exhibited suppressed swelling and improved conductivity while the membrane crosslinked with the conventional crosslinker of amin group decreased the conductivity significantly. In particular, the membrane modified by OXA (OXA/GOL) exhibited the most increased through-plane conductivity, 13.4 mS cm^{-1}, and the maximum power density, 261 mW cm^{-2}, of the H_2-O_2 fuel cell, because of the further increased oxygen content (O/C) of GO membrane by the crosslinking reaction with the oxygen functional groups. In addition, the fuel cell with OXA/GOL exhibited the excellent power generation stability at the elevated temperatures up to 50 °C suggesting a strong crosslinking connection with -COOH groups. Thus, the OXA/GOL membrane shows promising potential for PEMFC applications.

Chapter 4 summarizes the findings and conclusions presented in the individual chapters, providing a general overview and outlining future directions.