

# NEW INSIGHT INTO MICROSACLE TRANSPORT PHENOMENA IN PEFC BY QUANTUM MD

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## INTRODUCTION

Polymer Electrolyte Fuel Cell (PEFC) has been exclusively developed in recent ten years. The principle of the power generation in PEFC is briefly represented in Fig. 1. There are, however, still many possibilities to achieve the drastic improvement for PEFC performance. We should precisely understand the many kinds of microscopic phenomenon which construct the power product of PEFC, i.e. catalytic reactions on the electrode, ion and water transport through the electrolyte, and so on. In this study, we have succeeded to acquire the new insight into the molecular scale structure and dynamics of transport and reactions by theoretical simulation such as quantum molecular dynamics. The keynotes of our study are summarized in following sections.

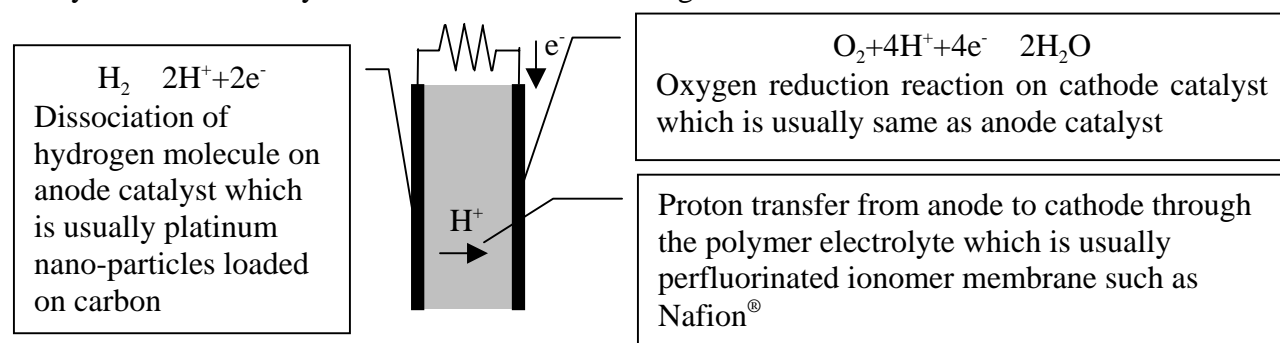


Fig. 1 Principle of power generation in PEFC

## OXYGEN REDUCTION REACTION ON CATHODE CATALYST

The oxygen reduction reaction has been considered as the most critical phenomena in PEFC. Many researchers have been estimated that the overpotential caused in this process corresponded to 70 % of the total energy loss. Although a lot of researches have been employed about this reaction, we cannot still get the clear insight about the reaction mechanism due to the difficulty of the direct observation. Such difficulty has prevented us from designing the optimal electrode structure. We have performed molecular dynamics simulations based on quantum mechanics that could quantitatively predict the chemical reaction including the complex electron structure changes without any experimental data<sup>1</sup>. The phenomenal results have been extracted from the dynamical simulation of the oxygen adsorption at the interface between water and platinum. Fig. 2 shows the bond length between oxygen atoms that had firstly existed as an oxygen molecule. The bond length has stretched step by step for 1 ps after the collision to the surface. The dissociation of oxygen atoms has suddenly occurred after such moderate stretching. We have not been able to find the any extraordinary behavior from only Fig. 2, but the unheralded phenomena have been observed from the relaxed structure of adsorbate on platinum surface, which has included the possibility of new principles about the optimal designing of the cathode electrode. We could find four adsorbed OH on the catalyst surface (Fig. 3). This means that the water

molecules reduced the adsorbed oxygen atoms.



We could acquire the clear picture about this reaction mechanism from the detail investigation of the dynamical process. Fig. 4 shows the mechanism of equation (1). The sequence proton transfer reactions between adsorbed water molecules and oxygen atoms have been observed, which could be represented as Grötthuss type proton transfer at the interface. We could expect that further reduction of these active OH adsorbates by protons would occur.



The water molecule acts as catalyst in the total reaction. These results indicate that the appropriate humidity of the interface cause more active catalysis reaction of oxygen reduction reaction.

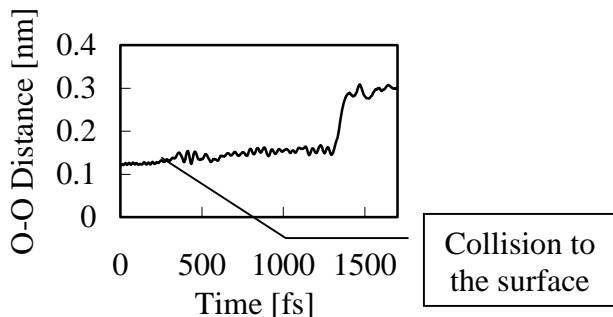


Fig. 2 Distance between oxygen atoms during the reaction

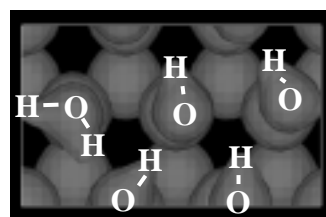


Fig. 3 Iso-surface of electron density of the surface at 1.6 ps

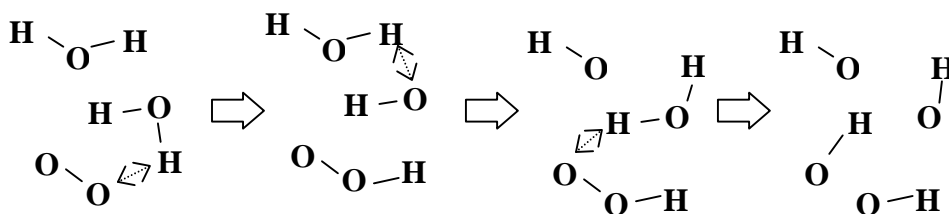


Fig. 4 Oxygen reduction by water molecules via Grötthuss mechanism at interface (Figure is drawn with perpendicular direction to the surface.)

## MASS TRANSPORT THROUGH POLYMER ELECTROLYTE

The unstable performance caused from the undesirable transport of ions and water through polymer electrolyte is a serious problem for PEFC performance, i.e. the increase of ohmic overpotential due to the resistance of the electrolyte, diffusion overpotential due to the insufficient supply of fuel and oxidant, and so on. It is demanded to elucidate the transport properties of the electrolyte and control the mass flux so that the optimal operation of PEFC would be achieved. In the previous studies, nano-structure of the electrolyte affected the mass transport properties and many researchers have confirmed the cluster formation by particles with polarization in the electrolyte, which would have corresponded to the transport path for ion and water (Fig. 5)<sup>2</sup>. Although we can draw such schematic figure, there is no smart method to answer the questions how hydrophilic

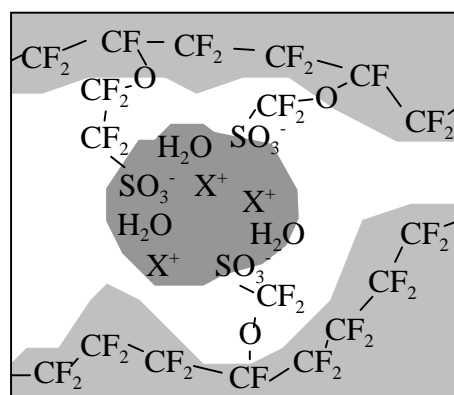


Fig. 5 Schematic figure of cluster formation in the electrolyte

clusters are generated and how mass transport occurs, such questions are important for the designing of the polymer which provides the high performance. We have developed the electrolyte model and employed classical style of molecular dynamics simulations for 1 ns<sup>3</sup>. We have succeeded to quantitatively predict the experimental diffusion coefficients of ion and water molecule. In addition, the nano-scale static and dynamical properties have been investigated. Fig. 6, 7 show the hydrophilic clusters generated in the simulation system. The 1-3 nm sized clusters that possess high tortuosity can be observed and particles with polarization move through this region. There are many narrow channels connecting these clusters and such region would have corresponded to the bottle neck point for mass transport through the electrolyte. Accordingly the intensifying the connection between clusters which means the high H-bond density in these region can provide the higher ion conductive electrolyte.

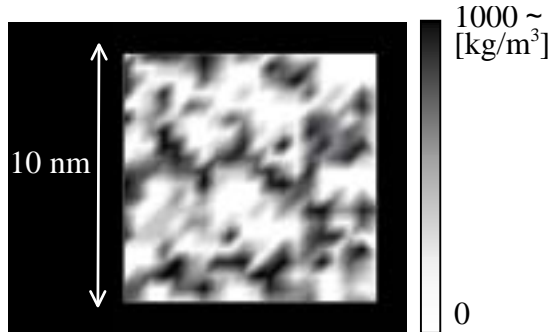


Fig. 6 Water density distribution

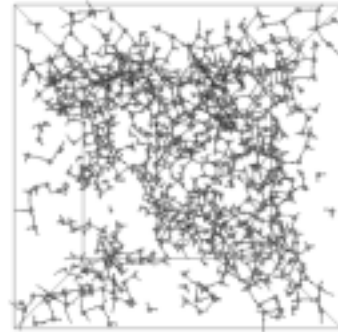


Fig. 7 Hydrogen bond structure

## CONCLUSIONS

We have acquired the novel knowledge from the molecular scale simulation studies about the oxygen reduction reaction on the cathode catalyst and mass transport through the polymer electrolyte.

### (1) Oxygen reduction reaction on cathode catalyst

The oxygen molecule adsorbed on the platinum surface has reduced by adsorbed water molecules and four OH have been generated in the quantum molecular dynamics simulation. This results indicate the possibility of catalysis by adsorbed water molecules at the catalyst and solution interface. Appropriate humidify of catalyst would cause the active reaction.

### (2) Mass transport through polymer electrolyte

We have developed the polymer electrolyte model and succeeded to quantitatively predict the transport properties of ion and water molecule. The hydrophilic clusters constituted by the particles with polarization have been generated in the simulation systems and this region possesses very tortuous structure. This region corresponded to the transport path for the ion and water molecule. Accordingly the designing of the polymer which generates the ordered hydrophilic clusters is considered as one of the most important guiding principles.

## REFERENCES

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