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Abstract (Doctor)

Title of Thesis	Development of solid-state ionic conductors and application to the polymer electrolyte membrane fuel cells
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Approx. 800 words

As a solution of the global warming caused by the greenhouse gases, fuel cell technology can be considered as one of the promising candidates of the energy resources. Among the several kinds of fuel cell, polymer electrolyte membrane fuel cell (PEFC) is main type of the fuel cells for the application to the fuel cell vehicle (FCV) due to the nature of PEFC such as compact, lightweight, and high-power density. In general, PEFC can be considered as the proton exchange type membrane fuel cell (PEMFC). However, full-scale market expansion of PEFC-derived technology has not been realized yet, due to the scarcity of Pt electrocatalysts resulting in high cost and concern about sustainability.

Variety kind of approaches were attempted to reduce amount of Pt use by enhancing catalytic activity or to seek an alternative catalyst, to solve the problem. Yet, the impact of material development of catalysts on solving problems is limited. In these circumstances, the two new drastic approaches, which are the changing the ion-conducting species transporting through the electrolyte membrane to OH^- and elevating the fuel cell operating temperature, were conducted in this study. In other words, investigation and development of new electrolyte membrane were conducted for realizing these approaches. PEFCs using OH^- conducting electrolyte membrane is called anion exchange membrane fuel cell (AEMFC). Under the OH^- ion conduction, the reaction in the fuel cell changed, resulting in the suppressed activation energy meaning that the reduced catalyst in need. As for the PEFCs operating under higher temperature, it is called medium temperature anhydrous PEFC (MT-PEFC). Since the conventional PEFC electrolyte, Nafion is limited to operate under 100°C due to the necessity of humidity, the electrolyte membrane for MT-PEFC is needed. Through the investigation on the ionic conductor and the examination of the application of prepared ionic conductor, the performance enhancement of the both AEMFC and MT-PEFC was confirmed. Furthermore, investigation on the composite proton conductor based on the acid-base interaction suggested that the theory to develop the proton conductor with high proton conductivity helping the future studies.

In the first and second research, improvement of hydroxide ion conductivity on the generally used potassium hydroxide-doped polybenzimidazole (PBI) by introducing layer double hydroxides (LDHs) showing high hydroxide ion conductivity was conducted for the performance enhancement of AEMFC. According to the results obtained by the physicochemical and electrochemical analysis, LDHs incorporation derived the improved water adsorbing property of the membrane, resulting in the high OH^- conductivity and less dependent on the humidity. Especially, PBI composite membrane with highest amount of LDHs (50 wt.% LDHs addition) showed maximum ion conductivity of 3.01 mS cm^{-1} at 60°C

and 80% RH. Finally, the prepared membrane with 30 wt.% LDHs exhibited the maximum fuel cell performance. For further improvement of AEMFC performance, I thought that controlling the nano/micro structural properties of LDHs is one of the approaches to achieve the better AEMFC performance in the aspect of the conductivity and dispersibility. The hydrothermal treatment which is the effective way to change the crystalline and bulk structure of LDHs was applied to sol-gel synthesized LDHs with different duration of time to investigate the morphological changes in the LDHs. As a result of the XRD and SAXS analysis, crystalline growth has two phases before and after 18h while the platelet structure growth contentiously pursuing for 48h.

Abovementioned studies have shown improved performance of AEMFC, but there are limitations to further improving performance. Thus, I focused medium temperature operation of proton exchange type PEFC as an alternative solution. In third research, the unique solution that incorporation of solid proton conductor into the catalyst layer, to reduce the activation overvoltage of MT-PEFC was introduced. In MT-PEFC, application of the anhydrous proton conductor to the catalyst layer to create the effective reaction mechanism is needed. Thus, cesium hydrogen sulfate (CHS)-silicotungstic acid (WSiA) composites which is previously reported in our laboratory was used as the solid ionomer. Not only suppression of the activation overvoltage but fuel cell performance enhancement was also confirmed under 150°C anhydrous condition by the CHS-WSiA ionomer. In fourth research, counter plan for the phosphoric acid (PA) leaching problem of conventionally used electrolyte, PA-doped PBI for the MT-PEFC was investigated. As a solution, reduced graphene oxide nanosheets (rGO NSs) was introduced to the PBI as a PA capturing fillers. The enhanced PA retention property was observed in the acid leaching test when 2 wt.% of rGO addition. Furthermore, proton conductivity of the PBI was improved probably due to the formation of proton conductive channel established by the adsorbed PA on the rGO surfaces, resulting in the improved power density of MT-PEMFC.

For the further enhancement of the MT-PEFC, I considered that the high proton conductive material for the medium temperature anhydrous operation not to depend on the PA doping which is potentially leaching, is essential. Thus, the proton conductive salt material with chemically fixed acid by acid-base interaction was examined. In the fifth study, I investigated the poly(4-vinylpyridine) based salt material reacting with several kinds of acids (PA, sulfuric acid: SA, nitric acid: NA, hydrochloric acid: HCl, acetic acid: AA, difluoroacetic acid: DFA and trifluoroacetic acid: TFA) to obtain the indicator to know high/low of proton conductivity of the salts. I focused on the protonated atomic distance (PAD) which is represented as the distance between nitrogen atom in the base and oxygen atom in the acid since the proton conduction in the salt is performed in between base and acid and calculated it using DFT. I confirmed that the PAD is strongly correlating with the proton conductivity, indicating that the PAD can be an indicator to evaluate the high/low of the proton conductivity. In the sixth study, we developed organic-inorganic salt proton conductor based on the heterocyclic imidazole with double acid-base interaction. Here, hydrochloric acid (HCl) and silanol group of the SiO₂ was oriented to the imidazole (Imi), then form the ImiHCl-SiO₂. $x\text{ImiHCl}-(100-x)\text{SiO}_2$ ($x=60$ wt.%) exhibited maximum proton conductivity of $1.4 \times 10^{-2} \text{ S cm}^{-1}$ at 130°C anhydrous. According to the theoretical investigation using DFT established in the previous part and physical characterization, promotion of proton dissociation in the system by the acid modification is the reason for the improved proton conductivity. In addition, MT-PEFC performance enhancement by incorporating ImiHCl-SiO₂ into PBI membrane was confirmed, achieving more than 520 mW cm⁻² which is high level among the relative studies.