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学位論文題名	Development of Highly Durable Cathode Catalysts for Protic Ionic Liquid Based Intermediate Temperature Fuel Cells (プロトン性イオン液体を用いた中温燃料電池のための高耐久カソード触媒の開発)
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【論文の内容の要旨】

Fuel cells have been getting much attention as one of the promising solutions for the emerging energy crisis. Particularly, low temperature polymer electrolyte fuel cells (PEFCs) have got much attention among the scientific community due to their properties such as high power density, energy efficiency etc. Besides these advantages, PEFCs have certain limitations such as CO poisoning of electro-catalyst, low reaction kinetics and difficulty in heat and water management at low operating temperature. Considering the high CO tolerance and enhancement of electrochemical kinetics at elevated temperature, fuel cells operating at intermediate temperature (>100 ^{0}C) are highly demanded . However the usual Nafion® electrolyte membrane cannot be used at elevated temperature since it requires hydration for proper proton conduction. Recently protic ionic liquids have been exploring as electrolyte for intermediate temperature fuel cells because of their properties like high ionic conductivity, high thermal stability and wide electrochemical window as well as negligible vapor pressure. Although, intermediate temperature PEFCs (IT-PEFCs) have been fabricated using protic ionic liquids such as N,N-diethylmethylammonium trifluoromethanesulfonate (dema-TfO), it is crucially important to study the electrochemical activity and stability of electro-catalysts at intermediate temperature in protic ionic liquids. So far no other catalyst except the expensive

platinum catalysts have studied as electro-catalyst in ionic liquids. Therefor it is very essential to explore the possibilities of non-noble catalysts to mitigate the use of expensive catalysts at intermediate temperature in dema-TfO.

The main scope of the present work is the development of efficient cathode catalysts and exploration of their electrtochemical activity along with the stability at intermediate temperature in protic ionic liquid (dema-TfO). In this dissertation, the *chapter 1* is devoted to the introduction part which explains briefly about the importance of IT-PEFC, physical and electrochemical properties of protic ionic liquid, dema-TfO and necessity of efficient electro-catalysts for elevated temperature fuel cells.

In *chapter 2*, I have studied the electrochemical behavior of commercially available platinum catalyst (Pt/C, 37.5 wt. %) at intermediate temperature in dema-TfO using rotating disc electrode (RDE). The durability test at 120 °C in dema-TfO shows 13 % loss of electrochemical onset potential as well as 56 % decrease of current density after 2000 cycle potential sweep suggesting that the Pt/C catalyst is not stable at elevated temperature in dema-TfO. This electrochemical results substantiated by comparing the TEM, EDS and Raman analysis data of Pt/C before and after durability test.

In *chapter 3* the synthesis and characterizations of non-noble hetero atom doped carbon catalyst, nitrogen doped graphene (NG) has been explored. The physicochemical properties of synthesized NG was examined using characterization techniques such as TEM, SEM, EDS, Raman, TG, BET and XPS and compared with reduced graphene oxide (RGO) and graphene oxide (GO). XPS shows 7.32 at.% of nitrogen incorporation on graphene plane, further more Raman, BET, TG and EDS analysis are also substantiate the presence of nitrogen doping by showing the characteristic difference from RGO and GO results.

Chapter 4 is doting the electrochemical studies of NG in two different electrolytes at two different operating conditions; 0.5 mol dm^{-3} H_2SO_4 at room temperature and dema-TfO at intermediate temperatures. The effect of operating temperature on ORR activity of non precious catalyst has also explored by doing RDE analysis in oxygen saturated dema-TfO at different temperatures suggesting that operating temperature has a crucial influence on the electrochemical activities of NG. The electrochemical stability of the NG was also studied in dema-TfO at 120 °C and the results shows the excellent stability of NG over Pt/C catalyst at intermediate temperature. TEM, EDS, Raman and XPS results taken after the durability test are also in agreement with the high durability of NG. Finally we have also optimized the

catalyst loading of NG in order to obtain the utmost activity. These remarkable electrochemical stability and activity of NG in ionic liquid indicate that nitrogen doped graphene can be a potential alternative cathode catalyst in ionic liquid for IT PEFCs.

Chapter 5 is focusing on the development of metal-NG (M-NG) composites (Pt-NG, Pd-NG & Fe-NG) to simultaneously improve the activity of NG and the stability of metal nanoparticle at elevated temperature in dema-TfO. The physicochemical characterizations such as XRD, TEM, EDS, XPS, Raman, BET and TG have carried out to get more insight in to the effect of metal incorporation on nitrogen doped graphene. *Chapter 6* is exploring the electrochemical activity and stability of M-NG in both aqueous acidic solution (room temperature) and dema-TfO at intermediate temperature. Interestingly all metal-NG composites show better electrochemical stability than Pt/C suggesting that NG is a promising catalyst support in dema-TfO at elevated temperatures. Pt-NG with very low Pt loading show better electrochemical activity and enhanced stability than Pt/C suggesting that Pt-NG is a highly promising cathode catalyst for ionic liquid based intermediate temperature PEFCs.