

論文要旨
Abstract of Dissertation

平成 30 年 03 月 26 日
Date: 18 Y 03 M 26 D

専攻 Department	Chemistry and Biotechnology
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論文題目 Title	Advanced Electroactive Materials Derived from Protic Salts and Protic Ionic Liquids for Energy Conversion Devices Involving Oxygen Electrode Reaction
和訳または英訳 Translation (J->E, or E->J)	プロトン性塩及びプロトン性イオン液体から成る電気化学活性材料の酸素還元反応を用いたエネルギー変換デバイスへの展開。
<p>Electrochemical energy storage and conversion devices such as – fuel cells can offer alternative solution to the current natural energy sources which have caused serious environmental impacts. The construction of catalyst layer which uses Pt or Pt-alloy covers the major cost of polymer electrolyte membrane fuel cells (PEMFCs) necessitating the development of non-precious metal catalyst as alternative such as- iron. Amongst the wide array of precursors and synthetic strategy, natural or synthetic polymers as carbonaceous precursors has become popular for designing advanced iron doped carbons. Apart from polymeric and macrocyclic complexes, 1,10-phenanthroline (Phen) as a sole precursor for iron doped carbons came into contention owing to the formation of a catalytic active site at high temperature at the edge of the graphene layer (phenanthroline type, Fe-N2-C4+) irrespective of the precursors reported few years ago. Due to the poor thermal stability of Phen, conventional approaches relied on foreign activating agent, supports or additives to yield high oxygen reduction activity and thereby increasing the complexity and cost of the processes. So, the candidate undertook the challenge of fabrication of an efficient oxygen reduction electrocatalyst from a molecular precursor like Phen via an inexpensive and robust platform without a laborious preparation process, additives and activation technique.</p> <p>In this study, the candidate has employed a protic salt, that is 1,10-phenanthroline dihydrogen sulfate ([Phen][2HSO4]) and iron halide (FeCl3) via nanocasting. The candidate has developed an in-depth understanding about the as synthesized iron doped catalyst by using series of spectroscopic techniques such as- Mössbauer, HR-TEM, XPS, XRD and ICP-AES etc. Under 14 wt% of iron loading and carbonization temperature of 900 oC, the prototype catalyst Fe14NDC-9 exhibited impressive activity in 0.1 M KOH. In contrast, Fe14NDC-9 exhibited inferior mass activity in 0.1 M HClO4. To improve the performance, Fe14NDC-9 was post treated by hot 2 M HCl to remove acid soluble, inactive inorganic particles and carbonized again at 900 oC to reduce the unstable functional groups (i.e., oxidized forms of carbon, nitrogen and sulfur etc.) at the graphene layer. After that, the catalyst named as Fe14NDC-9-W2M-9 displaying improved mass activity than Fe14NDC-9 under similar experimental conditions. The stability of the catalyst was assessed by chronoamperometry (i-t) and cyclic stability tests. Firstly, chronoamperometric analysis revealed higher retention of current density for Fe14NDC-9 (84.7%) than for Pt/C (77.5%). It was further improved for Fe14NDC-9-W2M-9 (87.9%) stressing the effect of post treatment. RDE voltammograms of Fe14NDC-9 exhibited 99.8% retention of the half-wave potential after 2000 CV cycles in O2-saturated 0.1 M KOH, which was comparable to the behavior of Pt/C (98.7%). In addition to this, Fe14NDC-9-W2M-9 also displayed high retention of current density and half-wave potential in 0.1 M KOH. On the other hand, in 0.1 M HClO4, Fe14NDC-9-W2M-9 showed higher retention (94.6%) of the half-wave potential after chronoamperometry at 0.7 V in contrast with Pt/C (91.4%). Also, active site responsible for the efficient oxygen reduction reaction has been explored and correlated with the mass activity in both alkaline and acidic solution. Interestingly, the candidate found that mass activity was dependent on the concentration of Nx-Fe and N-g (valley) which can act as a co-catalytic centre</p>	

in iron doped carbons. The candidate concluded that balance doping of Nx-Fe and N-g (valley) in iron doped carbons which could be controlled by simple synthetic parameters. The candidate also envisaged that careful design of cationic and anionic structure of protic salt and anion of iron salt could be vital to control over the active sites and thus to achieve highly efficient catalyst.

On the contrary, the current PEMFCs operate at 80 °C and requires humidification and the cathode catalyst, that is, Pt or its alloy get poisoned by CO. So, by increasing the functioning temperature (> 100 °C) of PEMFCs poisoning effect can be suppressed. In that regard, protic ionic liquids (PILs) have been coveted as the potential non-aqueous electrolyte and it has been previously reported that tertiary amine based PILs having only one transferrable proton has shown excellent oxygen reduction activity, for instance, diethylmethylammonium triflate, that is, [Dema][TFO]. But, such protic ionic liquids lacked high proton conductivity. In comparison with water, primary amines also have two protons in their functional group which makes them ideal system to consider for fuel cell applications. In this study, the candidate has attempted extensive series of primary amines with super strong acids such as- triflic acid (TFO), bistriflic acid (TFSA) etc. First breakthrough was obtained by using 2-Ethylhexyl ammonium cation with TFSI anion, that is, [2-Ehexa] [TFSI] which exhibited promising catalytic activity. Then, to understand their electrochemical behavior with respect to cationic structure, alkyl chain length was varied and following examples were, 2-Methylbutyl amine and 2-Methylpropyl amine formed corresponding PILs, that is, [2-Mbua] [TFSI], and [2-Mpra] [TFSI]. In terms of bulk properties, in general, such class of PILs showed lower thermal stability than tertiary amine ones measured by TG-DTA as the additional hydrogen bonds are much weaker in primary amine cation in PILs. Additionally, transport properties, such as- viscosity was measured by rheometer found to be much higher at room temperature due to the extensive hydrogen bonding exist in them, but reduced significantly with temperature rise and was comparable with isomeric tertiary amine based PILs at 120 °C. In fuel cell reactions, these novel PILs displayed high current density in comparison with their tertiary amine counterparts. Such phenomena only observed for PILs with excess base or acid in earlier reports. So, the candidate concluded that by keeping intact the activity, enhancement in proton conductivity could be achieved via primary amine based PILs.

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Maximum of 4,000 characters for Japanese or 2,000 words for European languages