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主　論　文　の　要　旨

論文題目　**Solution Plasma Synthesis of Heterographene for Energy Conversion System（ソリューションプラズマによるエネルギー変換用ヘテログラフェンの作製）**

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論　文　内　容　の　要　旨

Efficient electrocatalyst for the oxygen reduction reaction (ORR) have attracted widespread attention to accomplish optimal performance for application in energy conversion systems such as fuel cell (FC) and metal-air batteries (MABs). However, the catalysts on the cathode suffer from several critical obstacles, and the possible commercialization of FC and MABs is difficult due to the inherent sluggish kinetics and high overpotential in the ORR. Currently, platinum (Pt) and platinum supported on carbon materials (Pt/C) are regarded as the best issues to solve these problems because of a four-electron reduction pathway in ORR process but, prohibitive cost, low reserves, and methanol tolerance interrupt the development of the large-scale commercializationIn this regard, ongoing research efforts have been devoted searching to replace Pt with Pt-free catalyst with highly efficient performance, selectivity, and durability, such as non-precious metal supported on nanocarbons, or metal-free heterogeneous nanocarbons. Among them, the metal-free heterogeneous nanocarbons have been regarded as one of the most prominent alternatives for the ORR electrocatalyst when they incorporate heteroatoms (e.g. N, B, P, S, and I) into the carbonaceous skeleton.

Solution Plasma (SP), a non-equilibrium discharge in liquids at atmospheric pressure and room temperature, has emerged as a useful synthetic method for various nanomaterial such as nanoparticles, nanocarbons, heterogeneous nanocarbons, and transition metal-carbon composites. Among these nanomaterials, the most interesting achievement is the formation of heterogeneous

nanocarbons. However, the conventional SP synthesis is still at a beginning stage in the field of carbon fabrication and, especially, difficult to control the morphology, structure, and bonding configuration between carbon and the doped heteroatoms. To overcome these limitations, we have developed the tune-up SP system which is composed of a low-pass filter circuit to improve the discharge stability by controlling the current oscillations.

In Chapter 2, a low-pass filter circuit was introduced to increase the density and temperature of electrons involved in a non-equilibrium condition. The discharge properties of the solution plasma generated by conventional and low-pass filter circuits were characterized and comparatively analyzed. Filtration of the MHz range current oscillations, an increase in the maximum discharge current,and a higher stability of solution plasma were obtained by simply inserting a resistorcapacitor (RC) component in the circuit, which leads to the increases in the density and temperature of electrons. This novel strategy using a low pass filter circuit provides plasma stability and energy control during the discharge in liquid.

Applying a low-pass filter circuit in solution plasma synthesis, in terms of a tune-up solution plasma (SP) synthesis, Chapter 3 researches to the fabrication of nitrogen doped nanocarbons depending on a low-pass filter circuit. We suggest a tune-up SP synthesis based on a simple one step and cost-effective method to fabricate nitrogen self-doped graphitic carbon nanosheets (NGS) as an electrocatalyst. This novel strategy using a low pass filter circuit provides plasma stability and energy control during the discharge in pyridine, determining the graphitic structure of nanocarbons doped with nitrogen. Notably, NGS has the relatively high surface area (621 m2/g), and high contents of nitrogen bonded as pyridinic-N and pyrrolic-N with 55.5 and 21.3 at.%, respectively. As an efficient metal-free electrocatalyst, NGS exhibits a high onset potential (-0.18 V vs. Ag/AgCl) and 3.8 transferred electrons pathway for ORR in alkaline solution, as well as better long-term durability (4% current decreases after 10000 s operation) than the commercial Pt/C (22% current drop).

On the other hands, boron-carbon-nitrogen (BCN) ternary systems with graphitic phase have been highlighted for their novel structural and electronic properties. Interestingly, BCN hetoro-nanocarbons can be regarded as alternative low-cost metal-free electrocatalysts for oxygen reduction reaction (ORR). Hence, in chapter 4, using selected precursors a new strategy for the simultaneous synthesis of nanocarbon co-doped with heteroatoms was found. The synergetic effect of N and B in an uncoupling bond state improved the formation of new active sites for the ORR performance by changing the electronic structure of the base carbon. Meanwhile, when B and N are bonded together, the BCN catalyst contributes to a reduced ORR activity by forming a balanced electronic structure in carbon. The BCN nanocarbon with uncoupling bond state exhibits an enhanced ORR activity under alkaline conditions, with onset potential of -0.25 V versus -0.31 V for B/N coupling and 3.43 transferred electrons during the ORR. Although the ORR activity of the B/N

uncoupling nanocarbon was not as good as the typical Pt/C, the durability of this synthesized material (15.1 % current decrease after 20000 s of operation) was significantly better than that of the Pt/C catalyst (61. 5 % current drop under the same conditions). After durability test, the increase of the chemical states containing oxygen was higher for Pt/C than B/N uncoupling.

In summary, we suggest a novel route to synthesize hetero-nanocarbons using a tune-up solution plasma system. The proposed method gives several advantages over assembling of nanocarbons: (a) one-step process, (b) ambient reaction environment, (c) straightforward and easy setup, (d) cost-effective production, (e) possible large-scale of synthesis quantities, and (f) eco-friend fabrication. In particular, the tune-up SP synthesis provides stability during the discharge in liquid, influencing the synthesized nanocarbon characteristics. In detail, the electrochemical measurements demonstrate a comparable catalytic activity and superior stability to Pt/C in alkaline medium, so that a low cost and large scale of hetero-nanocarbons is a promising candidate for the next generation of electrocatalyst in metal-air batteries.