



Title	CONDUCTING POLYMER-FUNCTIONALIZED CARBON NANOTUBE MATRICES FOR ENHANCED PERFORMANCE OF BIOMASS BASED-FUEL CELLS
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## 論文内容の要旨

In this time of mankind's search for alternative energy sources, enhancement of the power gain from bio-fuel cells is a desired outcome and nanomaterial intervention can offer a good leap to that end. However, to fulfill that goal, scientists are struggling with the poison of catalysts by bio-fuels during oxidation reaction, the cost effectiveness, and the difficulty of fabrication processes.

In my research, conducting polymers and functionalized multi-walled carbon nanotubes (fMWCNTs) were used to support Platinum (Pt) as the anodic catalysts for the enhanced catalytic activity, poisonous tolerance and the utilization of Pt for cost effectiveness. During two and a half years, two of the most prospect biofuel cells were addressed as targets for our catalyst development: Bio-Hydrogen and Bio-Ethanol fuel cells. For the first type, a new design of biohydrogen fuel cell by integrating bioreactor for hydrogen production with anode chamber in hydrogen fuel cell was fabricated. Two different composites of platinum nanoparticles decorated on functionalized multi-walled carbon nanotubes (fMWCNTs) and polyaniline (PANI) were fabricated using the chemical and electrochemical polymerization methods. The biohydrogen fuel cell using PANI nanofibers deposited on Pt/MWCNTs/carbon paper as anode showed much higher power density than that used core-shell structure PANI/Pt/MWCNTs and Pt/MWCNTs without PANI. The differences in structure between these two composites and their effects on the interaction with hydrogen gas inside anode chamber leading to the difference in power density of fuel cell were also discussed. Further, the effect of conducting polymers' structural assembly on the enhanced performance of anodic catalysts was fully characterized by electrochemical studies. For Bio-Ethanol fuel cell, the fermentation process and application of the bio-fuel in direct ethanol fuel cell were separated into two individually processes. The first process has been done by the low temperature Teflon filtered system, which offers the bio-ethanol with optimized purity without distillation. The later one has been investigated by utilizing the conducting polymers and functionalized carbon nanotubes as the novel supporting matrices for Pt nanoparticles decorated on MWCNTs. To improve the electro-catalytic activity of Pt nanoparticles decorated on multi-walled carbon nanotubes (Pt/MWNTs) for ethanol oxidation, a co-assembled conducting polymer, polyaniline-poly(pyrrole) (PANI-PPY), was successfully employed for the first time. In native form, PANI and PPY individually deposited on Pt/MWNTs/C exhibited lower catalytic activities over

ethanol oxidation than the bare Pt/MWNTs/C. However, the co-assembled PANI-PPY deposited on Pt/MWNTs/C significantly enhanced both reaction kinetic and stability of catalysts compared to the one without conducting polymers as revealed from electrochemical measurements. These enhancements were attributed firstly to the active interface between Pt nanoparticles and conducting polymers, and secondly to the interaction between PANI and PPY and their contribution to the reaction on Pt surface. Based on the understanding from co-assembled PANI-PPY, we suggested that the functional groups on polymer backbone may play a crucial effect during ethanol oxidation reaction. To recognize their roles, MWCNTs was used as the highly conductive and chemically inert backbone to attach the desired functional groups. Thus, f-MWCNTs became the ideal tools for functional group effects' study to further explore the mechanisms existing within the matrix-effect.

We have chosen -COOH and -NH<sub>2</sub> groups since both of them could create the dissociative adsorption with water molecules via H-bonding and simultaneously induce charged non-covalent interactions. The results showed that the COOH-MWCNTs supported Pt/MWCNTs enhanced the ethanol oxidation reaction kinetics by three times higher than NH<sub>2</sub>-R-MWCNTs and the bare Pt/MWCNTs in terms of oxidation current density and stability. The results emphasize the important role of functional groups functionalized on supporting matrix for catalytic enhancement on Pt active sites. In addition, they provide data that clearly differentiates the effect of specific functional groups depending on their chemical species. Furthermore, various structural assemblies between f-MWCNTs and Pt/MWCNTs were studied and their impacts on kinetic reaction were analyzed. Infrared spectroscopy and dynamic light scattering measurements were carried out to investigate these specific interactions during and after sample preparation, while a number of electrochemical methods were used to investigate the enhanced catalytic activities and stability. Interestingly, the grafted structure had double the catalytic activity and stability than the multilayered structure loaded with the same amount of f-MWCNTs and Pt/MWCNTs. Further investigation on reaction kinetics and the effects of the ratio between f-MWCNTs and Pt/MWCNTs suggested that the catalytic performance of each structure depends strongly on the non-covalent interactions among functional groups, reactants, intermediates and the Pt active surface in the double layer region. These dependencies, in turn, are stronger for the grafted structure than the multilayered one. Based on the effects of changing reaction parameters, we propose that the grafted structure acts like a natural enzymatic catalyst while the multilayer structure performance resembles a conventional alloy catalyst.

These results provide important strategies for exploring ways to tune catalytic activities of organic materials-based catalysts, paving the way for future development of viable organo-metallic biomass based-fuel cells.

## 論文審査の結果の要旨

再生可能なエネルギー資源であるバイオマスを原料として直接電気エネルギーへと変換する燃料電池の研究がきわめて有用である。そこで本論文では、糖質などのバイオマスから微生物反応により水素やエタノールへと変換し、これらを直接電気エネルギーに変換するバイオマス燃料電池の開発をめざして、微生物リアクターとの連携によるシステム化や導電性ポリマーやカーボンナノチューブなどを用いた燃料電池電極の活性の向上を検討している。以下に、本論文における成果をまとめている。

1) 大腸菌などの微生物は、有機物から水素を直接生成することができるため、ここでは微生物が生産する水素を直接電気エネルギーに変換する水素燃料電池のアノード電極の活性向上と微生物リアクターと燃料電池を連結させた一体型のシステムの検討を行っている。まず、アノード電極としてカーボンナノチューブ上に白金ナノ粒子を形成させ、これに伝導性ポリマーであるポリアニリンを複合化することにより水素に対する吸着性を高め、水素燃料電池の出力の向上を実現している。特にポリアニリンをカーボンナノチューブ上に電解重合を用いて形成させることにより約 6 倍も出力向上を実現している。次にこの電極に水素を生産できる微生物（ここでは大腸菌）を培養可能な小型リアクター (20 ml) を気相を介して連結した。これを用いてグルコースを原料として微生物から水素生成し、新たに開発した燃料電池電極により 773 mW/m<sup>2</sup>の出力が継続的に得られている。

2) エタノール燃料電池は、低濃度 (2-5 % (w/w)) のエタノールでも作動させることができるため、微生物反応で得られるエタノールを濃縮せずに用いることが可能である。そこで、燃料電池のエタノールに対する出力の向上をめざして、アノード電極に白金ナノ粒子を形成させたカーボンナノチューブにポリアニリンやポリピロールの伝導性ポリマーを被覆することを検討した。その結果、両者のポリマーをほぼ同量比で形成させた際に、1.3 倍の電流密度の向上が得られている。特にポリピロールはエタノールの吸着を、ポリアニリンは生成物の脱着に寄与すると考察している。また、白金ナノ粒子を有するカーボンナノチューブにカルボキシル基やアミノ基などを化学修飾し、その影響を調べたところ、カルボキシル基を有するカーボンナノチューブを被覆した電極がエタノールの酸化を高めることが示されている。さらにカーボンナノチューブの電極上の配置についても微小な凝集構造を形成させることにより、より高い電流密度が得られることも見いだしている。

以上のように、本論文は、バイオマスから生成される水素やエタノールから直接電気エネルギーに変換を行う燃料電池に着目し、伝導性ポリマー、カーボンナノチューブ、白金ナノ粒子などの機能材料を電極上に 3 次元的に配置することにより、より多くのエネルギーを出力するための有用な知見を得るとともに燃料電池と微生物リアクターとの融合などについても試みたもので、応用物理学、特にナノバイオデバイス分野に寄与するところが大きい。よって本論文は博士論文として価値あるものと認める。