

Polymer Electrolyte Fuel Cell Electrodes from Chemical Vapor Deposition (CVD) Techniques-a review

Madhuja Chakraborty

Abstract— This review article deals with the Polymer fuel cell electrode growth using chemical vapor deposition techniques is reviewed. The supports, the nanocatalyst sizes, morphologies, and the resulting electrodes are examined as a function of the vapor deposition process; sputtering, CVD, plasma-enhanced (PE)CVD, and metal-organic (MO)CVD. In each case, up-to-date fuel cell performances are highlighted.

Index Terms— Catalyst, Electrode, Fuel cell, PEMFC, PVD, Thin film

I. INTRODUCTION

Low-temperature solid polymer fuel cells, such as proton exchange membrane fuel cells (PEMFCs), direct alcohol fuel cells (DAFCs), or solid alkaline membrane fuel cells (SAMFCs) are promising energy power supplies in the context of greenhouse-gas reduction. When powered with hydrogen and oxygen, the only by-product is warm water. The fuel cell is a direct current source issued from electrochemical conversion of fuel and oxidant (e.g., pure, or from air, oxygen)

at the two electrodes of the fuel cell. These two electrodes are separated by either a proton or anion (OH⁻) conducting solid polymer, forming a membrane-electrode assembly (MEA).

The electrodes are conventionally made of a microporous catalytic layer, a microporous gas diffusion layer (GDL) supported on a carbon backing (carbon cloth or carbon paper). The proton or anion exchange membrane is a polymer allowing ion conduction in wet conditions. These components are fabricated individually and then pressed together at high temperature and under high pressure.

The interface between the membrane and the electrode is critical.[1] The MEA is finally sandwiched by two flow field plates (bipolar plates) for efficient current collection and gas distribution.

Part of the optimization of an electrode design is the attempt to correctly distribute the amount of volume in the catalyst layer between the transport media for each of the three phases (electrons, protons, and gases) to reduce transport losses. This catalyst layer is either applied to the membrane or onto the gas diffusion layer. In either case, the objective is to place the catalyst particles (platinum, platinum alloys on non-based platinum) in close proximity to the membrane, the carbon particles, and the gas-fed pores.

Designing efficient electrodes remains a challenging task in

terms of increasing efficiency and stability, ensuring durability (for car application, at least 5000 h operation is required) and reducing costs (especially due to the noble metal catalysts).

Many methods are commonly employed to form the microporous catalytic layer.[2,3] Chemical synthesis, such as colloidal methods like water in oil micro emulsion carbonyl route, impregnation-reduction method, and electrochemical impulsion method, (from salts) allow the production of supported catalysts ready to be brushed onto the GDL. Progress in GDL manufacturing is also currently emerging.

In particular, one can mention the use of carbon aerogel that readily provides new carbon supports for fuel cell electrodes. Beside these methods, vapor deposition methods are of increasing interest for growing the catalyst support (usually carbon-based), placing the catalyst nanoclusters on the upper part of the electrode and/or for growing the full electrode as a thin film. The present article will briefly describe the current state of the art of these vapor techniques.

II. NEW CATALYST SUPPORT MATERIALS BY VAPOR DEPOSITIONS

CVD, in the field of low-temperature fuel cells, is mainly used to obtain nanostructured carbon (possibly porous) thin films as a potential alternative electro-catalyst support to replace traditional carbon black powder materials (i.e., Vulcan XC72 and Shawinigan carbon powders). Catalyst coating is further obtained either by salt impregnation (mainly electro deposition or electro less deposition) or by vapor deposition (mainly plasma sputtering). Two main types of nanostructured carbon supports are obtained by vapor deposition; arrays of carbon nanotubes (CNTs) and nanofibers (CNFs), and randomly nanostructured carbon thin films. Among the recent new materials are carbon nanohorns, nanosheets, boron-doped diamond, or transition metal oxides, however this short review will discuss only transition metal oxides.

A. CNTs and CNFs

Carbon nanostructures, such as CNTs (single-wall or multiwall) and CNFs are expected to provide the essential high surface area to be suitable as catalyst supports in a polymer electrolyte fuel cell electrode. In most cases, CNTs and CNFs are grown by catalytic CVD or PECVD. In the latter case, the CNTs and CNFs are grown at a lower temperature, and aligned nanostructures can be easily obtained. Precise growth conditions (precursors, temperature,

pressure, flows etc) depend on reactor geometry, properties of expected CNT, CNF (size, density, vertically aligned or not). Arrays of vertically aligned CNTs/CNFs are usually grown on macroporous carbon Paper or microporous GDL (as shown in Figs. 1 and 2)

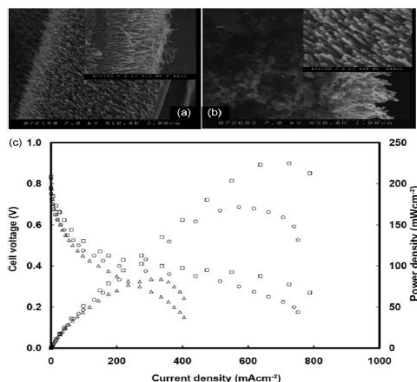


Fig. 1. a) Scanning electron microscopy (SEM) images of 2 μm long aligned CNF grown on a 5 μm diameter carbon fiber by PECVD with a close-up showing a side-view of the CNF array (reproduced from the literature^[23]). b) SEM images of 1 μm long CNF grown on a microporous GDL with a close-up showing the top view of the CNF array (reproduced from the literature^[23]). c) Cell voltage *E* versus current density *J* curves, and power density *P* versus current density *J* in a single, *cm*² surface area PEMFC with various Pt/C cathode structures: (○, △) cathode without GDL and with CNF, (□, ▽) cathode with CNF and diffusion layer, and (◇, ◊) cathode without CNF and with diffusion layer (reproduced from the literature^[23]). MEA assembly: cathode-sputtered Pt loading 20 μg/cm², commercial anode Pt loading 50 μg/cm², untreated Nafion[®] 115 membrane, hot-pressed MEA (130 °C for 120 s under a pressure of 40 kg/cm²). Operating conditions: cell temperature 80 °C, H₂/O₂ back pressure 3 atm. All figures reproduced with permission. Copyright 2007, American Institute of Physics.

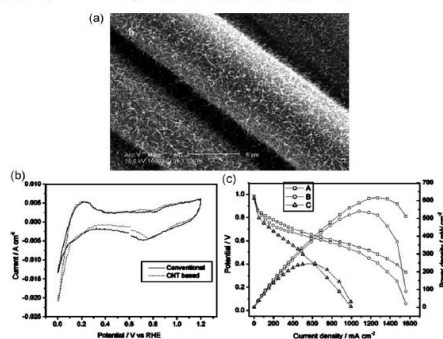


Fig. 2. a) SEM images of CNTs deposited directly on carbon paper by CVD (reproduced from the literature^[23]). b) In-situ current vs. voltage of both CNT-based and conventional electrodes at a scan rate of 50 mV s⁻¹ by supplying N₂ to the cathode side (serving as working electrode) and H₂ to the anode side (serving as counter and reference electrode) (reproduced from the literature^[23]). c) Cell voltage *E* versus current density *J* curves, and power density *P* versus current density *J* in a single PEMFC cell for: (○, △) CNT-based electrode, (◇, ◊) conventional electrode, and (□, ▽) CNT-based electrode without diffusion layer (reproduced from the literature^[23]). MEA assembly: Nafion[®] 115 membrane, hot-pressed MEA at 135 °C under 140 atm for 90 s. Pt loading for the commercial and CNT-based electrodes: 0.15 mg/cm². Operating conditions: cell temperature 70 °C, H₂/O₂ back pressure 3 atm. All figures reproduced with permission. (a) Copyright 2005, Institute of Physics. (b,c) Copyright 2005, American Institute of Physics.

followed by the catalyst impregnation. For simplicity and without loss of generality, only Pt is discussed here. The CNF/CNT array is subsequently catalyzed by electroless deposition, electrodeposition (by using Pt-based salts) and plasma sputtering.[23] In the two former cases, the full length of the CNTs/CNFs are decorated by highly dispersed Pt nanoparticles with a low degree of agglomeration. Deposition of Pt alloys (Pt_xRu_y) was also investigated, mainly for methanol DAFC operation.

NCNTs are grown by a modified CVD process in a nitrogen-rich gas mixture. The Pt nanoparticles deposited by aerosol MOCVD, are uniformly dispersed on the NCNT, and have narrower particle size distributions, whereas the average Pt particle size is larger with a broader particle size distribution on the CNT support.

B. Mesoporous Carbon Thin Film

CVD and PVD have recently been applied to the synthesis of a three-dimensional porous carbon thin film matrix to support, or to embed, Pt catalyst nanoclusters. By combining these techniques with another vapor deposition technique, a large range of catalytic layers can be synthesized.[42] Among the various forms of mesoporous carbon thin films, ordered mesoporous carbon (OMC) is of

great research interest, especially for electrochemical applications such as fuel cells (lithium ion batteries and capacitors).[30–33] By using a suitable template, such films offer prominent characteristics such as high surface area, tunable and uniform pore size, ordered pore structure, interconnected pore network, tailorable surface properties, and good mechanical stability. CVD is one of the most used techniques to synthesize such films because of the high degree of pore filling, the formation of graphitic pore walls, the presence of crystallite-sized graphite, and the possible absence of a dense carbon layer on the external surfaces of the template. The use of OMC leads to higher performance in electrochemical activity than commercial carbon black particles, especially in DMFC. This enhancement is attributed to the uniform mesopore network in OMC which seems to improve the diffusion of the reactants, and the high electrical conductivity of the graphitic OMC.

C. Transition Metal Oxides

Transition metal oxides, such as ZrO₂, SnO₂, RuO₂, TiO₂, have been applied to improve the durability of the carbonsupported platinum catalysts and the Pt activity for the oxidation reaction of organic molecules (by lowering the adsorption energy of CO). It was recently reported that the active surface area of the platinum in the Pt/TiO₂/C has been reduced. Very few studies are devoted to vapor deposition of Pt/TiO₂/C catalysts. Using radiofrequency (RF) magnetron sputtering, recently researchers have synthesized PtRu nanoparticles embedded in a TiO₂ matrix for methanol oxidation with various sizes of PtRu nanoparticles and indicate that the activities of the methanol oxidation reaction are dependent on the PtRu particle size. The high catalytic activity of PtRu/TiO₂ is partially attributed to the effect of the TiO₂, on which the hydroxyl (OH) species are absorbed. This causes a shift in the surface oxidation of PtRu which facilitates the removal of CO from the PtRu nanocatalyst surface, and reduces the poisoning of the Pt in the PtRu/TiO₂ thin film.

III. EFFICIENT CATALYST NANOCCLUSERS BY VAPOR Deposition

Two techniques are commonly used to synthesize efficient catalyst nanoclusters for a low-temperature fuel cell. Plasma-sputtering deposition was investigated for its ability to reduce the noble catalyst content in PEMFC electrodes in order to reduce fabrication costs while preserving fuel cell performance. E MOCVD provides an alternative way of depositing efficient catalyst nanoclusters onto gas-diffusion layer electrodes.

The basic principle of plasma sputtering is to sputter a catalyst target with the plasma ions, e.g., argon. The sputtered atoms condense on a substrate located a few centimeters from the target. This substrate can be the gas diffusion layer, or the polymer electrolyte for direct deposition. Plasma sputtering can be readily used for depositing only the catalyst of both the catalyst and the electron-conducting matrix (mainly carbon) as described in the catalyst content and eventually increasing the PEMFC

efficiency, are given. Among them, Cha et al.[45] and Haug et al.[49] have deposited alternate sputtered platinum layers and painted layers of Nafion1 and carbon ink (NCI) directly onto the membrane.

MOCVD is intended to allow deposition of noble metal catalysts onto gas-diffusion layer electrodes rather than using conventional chemical methods.[52–56] It is a suitable method for impregnating tortuous electrode supports, as shown in Figure 6a. Recent experiments have shown interesting oxidation reduction reaction behavior. For a Pt cathode loading of 100 mgPt cm⁻², the maximum power density, shown in Figure 6b, is about 800mWcm under H₂/O₂ conditions (4 bar and 80 °C) with a Nafion1 112 membrane.

IV. CONCLUSION

This short review paper is aimed at presenting both CVD and plasma-sputtering deposition techniques in the field of improvement of fuel cell electrodes as an alternative to conventional or original chemical impregnation methods. All the presented methods are successfully used to build efficient fuel cell electrodes. Plasma sputtering combines the advantages of depositing pure catalyst and/or carbon atoms without any additional bonds lowering the catalytic activity. It is also advantageous for controlling catalyst distribution near the electrolyte polymer membrane, and the mean size distribution. High fuel-cell efficiency, 20 kW/g

REFERENCES

- [1] C. Wang, M. Waje, X. Wang, J. M. Tang, R. C. Haddon, Y. Yan, *Nano Lett.* 2004, 4, 345.
- [2] X. Wang, M. Waje, Y. Yan, *Electrochem. Solid-State Lett.* 2005, 8, A42.
- [3] M. M. Waje, X. Wang, W. Li, Y. Yan, *Nanotechnology* 2005, 16, S395.
- [4] M. Sudan Saha, R. Li, X. Sun, S. Ye, *Electrochem. Comm.* 2009, 11, 438.
- [5] A. Caillard, C. Charles, R. Boswell, P. Brault, Ch. Coutanceau, *Appl. Phys. Lett.* 2007, 90, 223119.
- [6] A. Caillard, C. Charles, R. Boswell, P. Brault, *J. Phys. D* 2008, 48, 185307.
- [7] Y. Shao, G. Yin, Y. Gao, P. Shi, *J. Electrochem. Soc.* 2006, 153, A1093.
- [8] Z. Tang, C. K. Poh, K. K. Lee, Z. Tian, D. H. C. Chua, J. Lin, *J. Power sources* 2010, 195, 155.
- [9] F. Alcaide, G. Alvarez, O. Miguel, M. J. Lázaro, R. Moliner, A. López-Cudero, J. Solla-Gullón, E. Herrero, A. Aldaz, *Electrochem. Comm.* 2009, 11, 1081.
- [10] H. Rabat, P. Brault, *Fuel Cells* 2008, 8, 81.
- [11] H. Rabat, C. Andreatza, P. Brault, A. Caillard, F. Béguin, C. Charles, R. Boswell, *Carbon* 2009, 47, 209.
- [12] A. Zakhidov, R. H. Baughman, Z. Iqbal, C. Cui, I. Khayrullin, S. O.

The self author, **Madhuja Chakraborty** is a final year student (4th year) of B.tech in Biotechnology in Heritage Institute of Technology, Kolkata, affiliated to Maulana Abul Kalam Azad University of Technology (formerly known as West Bengal University of Technology). Madhuja also has commendable contributions to scientific research in different laboratories.