

CARBON MATERIALS FOR MICROELECTRODES IN FUEL CELLS

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1. Introduction

One of the most interesting developments in electrochemistry of the last decade is the conversion of chemical energy into electricity via fuel cells.

Of the various fuel cells being considered, the direct methanol fuel cell (DMFC) is very attractive due to the key advantages of system simplicity and good transient response compared to reformed-air fuel cell systems. The overall objectives of the effort is to develop new low-cost electrocatalyst materials and new methods of preparing fuel cell electrodes that will reduce the amount of noble metal used and lead to overall cost reduction with improved performance [1]. Methanol fuel cells are increasingly being considered for low to medium power application due to the elimination of the fuel re-processing, reduced weight and volume, and simple system design and operation. However, there are some limitations such as; the operational temperature, sluggish methanol oxidation kinetics and methanol cross over through the membrane electrolyte.

There are two reasons why anodes of DMFC need to have internal structures different from cathodes of PEMFC: the wetting nature of methanol and its larger molecular size (compared to hydrogen) and the fact that the gaseous product CO_2 has to be removed from the catalyst sites and the electrode pore system [2].

For practical anodes of a DMFC, the electrocatalyst is deposited on a carbon support. Carbon is an ideal material for supporting nanosized metallic particles in the electrode for low-temperature fuel cells, such DMFCs and PEMFCs. No other materials except carbon materials have the essential properties of the electronic conductivity, corrosion resistance, surface properties and the low cost required for the commercialization of fuel cells. The requirements of carbon materials for their applications to the supports for metallic-based electro-catalyst counted as follows. A high surface area for a high level of nano-sized catalysts dispersed. A good crystallinity and low electrical resistance to facilitate the electrons transport during the electrochemical reactions. A suitable pore structure for maximum fuel contact and by-products releasing must be accommodated. The interactions between the catalyst nanoparticles and the support should be reduced [3]. The electrodes with supported catalysts play an important role in the mass transport of the fuel cell. A well-dispersed catalyst can lead to substantial improvement in the performance of DMFCs.

It is extremely difficult to design and synthesize carbon materials with all given characteristics, but in terms of design and application of a catalyst support in fuel

cells, novel carbon materials, that possess a high surface area, a well defined porosity and a good electronic conductivity, represent an attractive goal.

Actually, the research is focused on nanostructured and architected carbonic materials with properties dependent of direction: 1. Pore distribution and micro channeling for fuel transport should correspond to a microfluidic with very high permeability; 2. The residence time to catalyst nanoparticles should be in accommodation with the membrane permeability and perpendicular on fluid transport; 3. The electrode must have high electrical conductivity.

Different carbon materials satisfy part of these requirements:

Carbon nanotubes have been intensively studied in various areas [3], particularly in catalytic supports, electrodes and nanocomposites. Carbon nanotubes are considered potential support, especially catalyst to be employed in liquid-phase reactions, owing to their mechanical and unique electrical properties. Current investigations are focusing on template–synthesis methods for highly ordered nanoporous arrays of carbon that showed better electrical activities of cathode oxygen reduction in a half-cell configuration [4].

Graphite nanofibers (GNF) have also been considered as a potential support for electrocatalyst and better activities of electrochemical oxidation of methanol were obtained in a cyclic voltammetry study [5]. The performance of the DMFC with Pt-Ru/herringbone GNF nano-composites, as anode catalyst, was enhanced by 50 % relative to that recorded by unsupported Pt-Ru colloidal anode catalyst [6,7].

Fullerene- nanofibers are the nanoscale fibers that consist of fullerene molecules and organic derivatives of fullerene molecules. They can be fabricated by the liquid-liquid interfacial precipitation method as in reference [8] and have a high thermal stability give rise to very porous by suitable heat treatment. These materials are expected in use as catalyst carriers in fuel cells.

Carbon nanofoams are new materials with many of the properties of traditional aerogels that are being used as electrodes for water deionization cells, fuel cells, and other devices and are superior to woven carbon fiber electrodes in many applications because of their high surface area, low resistance and high relative capacitance [9].

Metal-coated carbon nanobeads on a porous ceramic are promising options for fuel cell electrodes. The ceramic substrate provides strength to the electrodes as well as porosity for good diffusion of the fuel/oxidant. Apart from an ability to assist in electron transportation, the nanobeads can be electroplated with metal particles to provide good activation of gaseous species [10].

Methanol is an attractive fuel for fuel cells, rather than H₂, due to its higher power density (liquid state), easy handling, storage and transport. There are two ways to use methanol as fuel. The first is to decompose it catalytically and use hydrogen-rich reformatted gas. The second option is to oxidize methanol directly on the anode. Methanol oxidation is a slow reaction that requires active multiple sites for the adsorption of methanol and the sites can donate OH species for the desorption of the adsorbed methanol residues [11].

One of the key points to develop a DMFC is to investigate new electro-catalysts for the oxidation of methanol at the anode, allowing the current density increasing and to decrease the anodic over voltage. Pt is the best catalyst anode for hydrogen oxidation, but in the presence of methanol, CO, formed as a reaction intermediate, irreversibly absorbs to the Pt surface, rapidly lowering its activity. Several studies have

shown that the best electrocatalyst for methanol oxidation is a platinum-ruthenium system, with Ru who serves the role of removing CO_{abs} as CO₂ (gas).

However, multiple efforts are devoted towards the development of new catalyst as methanol oxidation catalyst of high activity. Research is focused on binary Pt and Ru catalysts, with little attention on ternary or quaternary catalysts; some promising results have been reported for Pt-Ru-A systems (where A = MoO_x, WO_x, VO_x, IrO_x). Nobel-metal based catalysts show a better activity and less carbon deposition than non-noble metal systems. Metal support interaction, dispersion and particle size have been found to be key factors in defining the ability of the solid to catalyze both the desired reaction and the carbon deposition [12].

The methanol is reforming using electro-oxidation to produce a hydrogen-rich gas stream containing carbon dioxide and carbon monoxide. PEMFC stack operating temperatures of around 80°C, the membrane electrode assemblies (MEAs) within the stack cannot tolerate such high CO levels and catalytic oxidation must reduce the CO content to less than 100 ppm, and in some cases down to a few ppm [13]. It is well established that bimetallic systems, with Pt as one of the components, give substantial tolerance compared to Pt alone, to the presence of CO in the fuel stream. Another noble metal with catalytic activity is Pd, a very good electrocatalyst for organic fuel electro-oxidation [14] and has the remarkable ability to store and release substantial amounts of hydrogen [15].

A relative ratio of the catalyst sites poisoned by carbon monoxide given in [16] indicated for a series of catalysts, tested different values of poisoning after CO saturation. The surface of the Pt particles for Pt/C remains fully blocked by CO, the CO coverage decreases with increasing Pd content. This corresponds to the observed decrease of CO oxidation charge, both consistent with the reduction of the saturation coverage of CO on Pd.

To avoid the platinum catalyst poisoning an intermediate layer with Pd is beneficial due to affinity to hydrogen and low capacity in poisoning with CO.

Another thing is that Pd could increase the proton transfer through PEM by hydrogen accumulation at interface associated with high mobility.

In this context, the objective of this work was to obtain new carbon materials for microelectrodes in fuel cells with higher conductivity and low polarization. The paper presents investigations to improve some physical-chemical characteristics of these electrodes (such as electrical conductivity, the rate of fluid diffusion/migration) and the assay to develop and optimize a new class of non-Pt model catalysts. The electrode structure and composition were determined by XRD and AFM analysis. Optical microscopy and SEM explored the electrode structure after catalyst deposition. Electrical conductivity of the carbon electrodes and rate of liquid diffusion through these materials were measured using homemade equipments.

The overall results clearly indicate better characteristics and performance for these electrodes.

2. Experimental

2.1 Electrodes

The starting materials: *novolac*, resin type phenol-formaldehyde condensation, crosslinked agent called hexamethylenetetramine (HMTA), silicon powder and poly-

acrylonitrile (PAN). Bulk samples were investigated. The electrodes consist of carbonized novolac with HMTA, carbonized novolac and Si with HMTA, carbonized PAN, where fuel is transported to catalyst (Pd) through micropores.

The mixture for the bulk samples were novolac and HMTA 10%wt or novolac, HMTA 10% and Si 10%wt (reported at novolac resin) have been ultrasonically homogenized in methyl alcohol with a subsequent drying for 24 h at 70°C in air. The samples were preformed by press forming in thin pellets after drying and mincing. All pellets were hardened and pyrolyzed up to 900°C as described in reference [17].

PAN was preformed by pressing in a thin pellets and thermal treated similar with procedure used for PAN-carbon fibers. All samples in final stage were mechanical polished for catalyst deposition.

Sample	Cod	Hardening temperature (°C)	Pyrolysis temperature (°C)
Novolac resin with HMTA 10%wt	NH10	300	900
Novolac resin with HMTA 10%wt and Si 10% (reported at novolac resin)	NHSi10	300	900
Polyacrylonitrile	PAN	-	900

2.2 Carbon-supported Pd electrode catalyst

One way to prepare electrocatalysts with a lower precious metal loading and a higher availability of the reactants to the catalytic sites is directly deposition of the catalyst into the porous structure electrode by chemical method. The catalyst deposition was performed by chemical reduction using a specific composition of PdCl₂ and NaCl. PdCl₂ was dissolved in distilled water to obtain a solution in the concentration of 0.006M. NaCl was dissolved in distilled water to obtain a solution in the concentration of 1 M. Equivalent parts of 0.006M PdCl₂ and 1M NaCl was mixed. Adding HCl the pH of the solution was adjusted to 0-2. Multiple immersing and washing of the electrode in the reduction solution performed the deposition.

3. Results and discussion

3.1 Physical characteristics

Electrical properties were investigated by resistance measurements on direct polished pellets before catalyst deposition.

Samples	$\sigma 10^3$ (S cm ⁻¹)
NH10	7.1
NHSi10	13.5
PAN	36.1

The permeability of the methanol, in pyrolyzed materials has been measured by immersion in alcohol and counted the mass in time. The measurements were accomplished to constant temperature. The phenomena were followed like a reaction of first order and the equation (1) give the rate of the fluid penetration.

$$\frac{dQ}{dt} = k(Q_{\max} - Q), \quad Q = \frac{m - m_0}{m_0} \quad (1)$$

The graphic representation:

$$\ln(Q_{\max} - Q) = f(t) \quad (2)$$

gives rise to the migration/diffusion rate, $K \text{ (s}^{-1}\text{)}$, which values were plotted in Fig1.

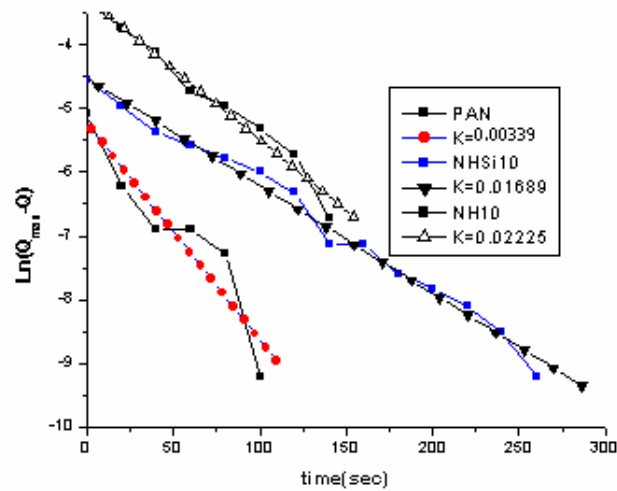


Figure 1.

A high mobility of methanol is observed for NH10.

3.2 Morphological and structural investigations

Atomic Force Microscopy, X-Ray Diffraction, Optical Microscopy and Scanning Electronic Microscopy have investigated the structural features at different organization levels.

AFM shows high roughness surface (Figure 2a) and catalyst is deposited in stacked flakes-like structures (Figure 2b)

XRD profiles of PAN, Novolac powder, NH10 and NHSi10 are shown in Figure 3. Beside characteristics peaks of turbolayers structures, at NHSi10 appear some supplementary peaks indexed in table 3.

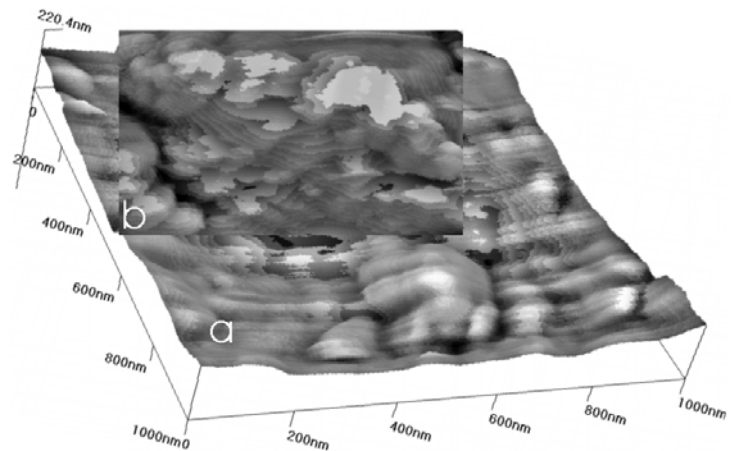


Figure2. AFM images of pyrolyzed PAN (a) and pyrolyzed PAN with deposited catalyst (b)

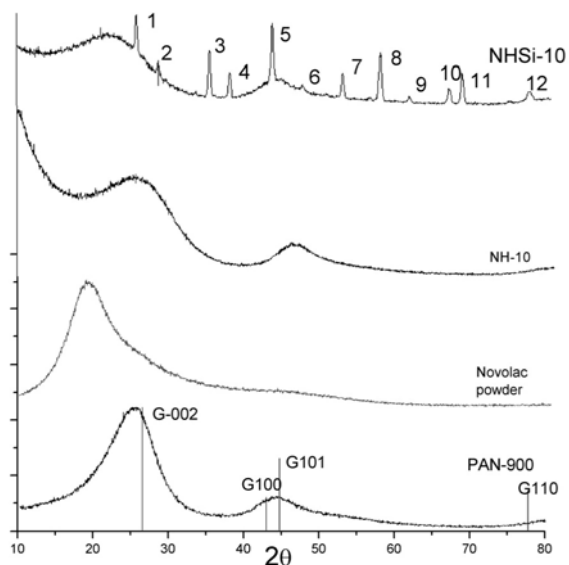


Figure 3. XRD profiles for PAN, Novolac powder, NH10 and NHSi10

Table 3. Supplementary peaks indexing of NHSi10

Peak No.	Experimental		Theoretical						Observations
	NHSi10		SiC ₂ : a=3.07 Å, c=7.02 Å			Glitter: a=2 Å.53, c= 5.98 Å			
	d(Å)	2θ	hkl	d(Å)	2θ	hkl	d(Å)	2θ	
1	3.47	25.6	002	3.51	25.4				Al ₂ O ₃ (d=3,48)
2	3.15	28.4							Si (d=3,13)
3	2.54	35.2				100	2.53	35.5	Al ₂ O ₃ (d=2,55)
4	2.38	37.8	003	2.34	38.4	011	2.33	38.6	Al ₂ O ₃ (d=2,38)
5	2.08	43.4	111	2.07	43.6				Al ₂ O ₃ (d=2,09)
6	1.93	47.35				102	1.93	47.04	
7	1.74	52.6	004	1.75	52.1				Al ₂ O ₃ (d=1,74)
8	1.60	57.5	113	1.59	57.9				Al ₂ O ₃ (d=1,62)
9	1.51	61.35	201	1.49	61.8				
10	1.40	66.55	022	1.40	66.4				
			005	1.40	66.6				
11	1.37	68.25	210	1.37	68.3				Al ₂ O ₃ (d=1,37)
12	1.23	77.2				021	1.23	77.0	Al ₂ O ₃ (d=1,23)

The catalyst was examined with optical microscopy (OM) and scanning electron microscopy (SEM). A set of OM images of samples before and after catalyst deposition and SEM images of carbon-supported catalyst, illustrates the variations of structure in Figure 4. There is a conglomerate distribution for PAN, irregularly and punctually distribution for NH10, inhomogeneous and anisotropic for NHSi10.

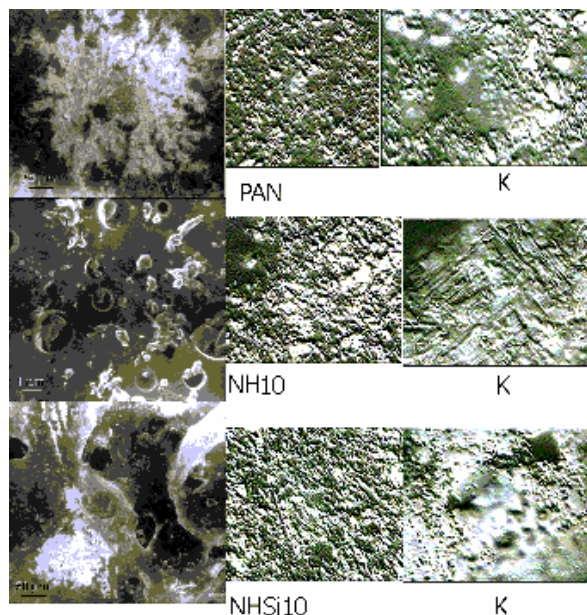


Figure 4. SEM (left), samples with catalyst deposited, OM images electrodes and deposited (K-catalyst).

4. Conclusions

Carbonic materials, obtained by carbonizing novolac and PAN are potential competitors for electrodes in micro direct methanol fuel cells. All materials examined in the present study shown that the conversion of novolac and polyacrylonitrile at 900⁰C and chemical catalyst deposition can be proposed as an another route for the electrodes for fuel cells having good physical properties. The surface morphology, porous structure, is close to requirements need a satisfying adsorption of fuel and release of by-products. In particular, NH10 showed the highest rate of the fluid penetration and PAN is the best conductive. In seems premature to draw far-ranging conclusions regarding the potential activity for methanol oxidation and mass transport properties of the palladium catalyst layer. The activity of carbon-supported Pd can be further improved by increasing the catalyst dispersion.

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