

Nanostructured Electrocatalytic Pt–Carbon Materials for Fuel Cells and CO₂ Conversion¹

S. Perathoner^{*a,b}, M. Gangeri^{a,b}, P. Lanzafame^{a,b}, and G. Centi^{a,b}

^a Dipartimento di Chimica Industriale ed Ingegneria dei Materiali, University of Messina,
Salita Sperone 31, Messina, 98166, Italy

^{*e-mail:} perathon@unime.it

^b European Laboratory of Catalysis and Surface Science (ELCASS)

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Abstract—The recent growing possibilities for the preparation, in large quantities and at low cost, of a number of different types of nanostructured carbons (carbon nanotubes, nanofibers, nano- and meso-porous materials, nanocoils and nanohorns, etc.) have open new possibilities in a range of applications: H₂ storage, electronic and field emission devices, advanced sensors, polymer reinforcement, and catalyst support. Nonetheless, most authors consider the use of these advanced nanostructured carbons with respect to carbon black only for the possibility of improving metal dispersion and/or utilization. However, these nanostructured carbons offer several additional aspects that make them highly interesting to develop advanced electrocatalysts.

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In this study, we give an overview of these general aspects focusing attention on two specific research trends: PEM fuel cells and the conversion of CO₂.

1. INTRODUCTION

Carbon nanotubes (CNT) and carbon nanofibers (CNF) have been intensively studied for a range of applications: H₂ storage, electronic and field emission devices, advanced sensors, polymer reinforcement, and catalyst supports [1, 2].

However, surprisingly little attention has been dedicated to their application in the preparation of advanced electrocatalysts, although the interest is rapidly increasing in parallel to the increasing attention to the development of improved PEM (proton exchange membrane) fuel cells.

Proton-exchange membrane fuel cells (PEMFCs), due to the low weight, fast start-up, and high power density-to-volume ratio, have received great attention in recent years especially for distributed applications, but their commercialization requires further improving of their efficiency and energy density. PEMFCs are typically prepared by supporting the catalyst (Pt) in the form of small particles on carbon black and then depositing this electrocatalyst over a macrostructured support (carbon cloths) which is then hot-assembled with the proton-exchange membrane (such as Nafion[®]) eventually by also adding a porous hydrophobic layer (such as Teflon[®]). While usually research has been focused on the role of the metal particles and

cell engineering, we have recently reported that the nanostructure of carbon, and not only its conductive characteristics, has a significant influence on the performances of PEM fuel cells [3].

The requirements of carbon materials for their application as a support for Pt-based electrocatalysts [4] are the following: a high surface area for a high dispersion of the nanosized catalyst, excellent crystallinity or low electrical resistance to facilitate electron transport during the electrochemical reaction, a pore structure suitable for maximum fuel contact and byproduct release, and good interaction between the catalyst nanoparticles and the carbon support.

Nanostructured carbons offer several aspects which make them highly interesting to develop advanced electrocatalysts: (1) the unique electrical properties of these materials which limit the charge of the supported metal particles, (2) the improved mass-transfer and three-phase boundary due to the presence of an ordered structure, (3) the possibility of preferential crystallographic orientation of the supported metal nanoparticles, (4) the confinement effect inside nanotubes, (5) the possibility of oxide/carbon combination to improve the performances and/or reduce sensitivity to poisoning, and (6) the possibility to develop hierarchically organized structures (on the nano-, meso-, and microscale).

We will discuss here the electrocatalytic activity in hydrogen oxidation of novel nanoengineered anodes based on a hierarchically organized structure: Pt nanoparticles are deposited on carbon nanotubes (CNT) or carbon nanofibers (CNF), which are grown directly on carbon cloth (carbon macrofibers). Their performances are compared with those of a reference commercial

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Pt/carbon black electrode from E-TEK. The analysis of their performances and their advanced characterization by TEM and SEM allow us to derive some relevant indications on the role of carbon nanoarchitectures in PEM anodes. In fact, the nanoarchitecture of carbon and the type of metal–carbon interaction, which in turn is also influenced by the carbon nanoarchitecture, determine the possibility to have an efficient formation of the three-phase boundary (gas–electrode–electrolyte) and an improved interaction between metal particles and the conductive carbon substrate. Both contribute in improving the efficiency in the chemical-to-electrical conversion, an important target towards the development of PEM fuel cells. Therefore, a better understanding of the role of carbon nanoarchitecture in the performance of PEM fuel cells is of key relevance for their improvement.

The second case discussed in this study concerns the behavior of nanostructured platinum–carbon based electrocatalysts for the conversion of CO_2 to Fischer–Tropsch hydrocarbons at room temperature and pressure.

A very attractive possibility to reduce the concentration of CO_2 , one of the main gases responsible for the “greenhouse effect,” is the gas phase electrocatalytic reduction of combustion products back to fuels [5]. This reaction represents one side of the PEC (photoelectrocatalytic) reactor [6–8] in which one side is composed of a titania-based photocatalyst which oxidizes water to O_2 using solar light-producing protons and electrons; these are transported, by a proton exchange membrane (Nafion®) and an electric connection, to the other side where they react with CO_2 in the presence of an electrocatalyst to produce hydrocarbons and alcohols.

A critical aspect is the development of an electrocatalyst that should be active at near room temperature to promote multielectronic reactions such as the transformation of carbon dioxide with hydrogen to hydrocarbons, avoiding side reactions that lead to H_2 and CO formation. It is expected that multielectron transfer reactions are favored by catalysts with high electron density, thus with a high number of surface atoms against bulk metal. In fact, in noble metal nanoclusters [9], a large percentage of metal atoms lies on the surface, and, moreover, the electrons in nanoclusters are confined to spaces that can be as small as a few atom-widths across, giving rise to quantum size effects.

Reported in this work is the behavior of electrocatalysts based on Pd and Pt nanoclusters deposited on a hydrophobic carbon cloth and jointed with a Nafion membrane in the room temperature gas-phase reduction of CO_2 .

2. EXPERIMENTAL

2.1. Preparation and Characterization of the Electrocatalysts for Fuel Cells and CO_2 Conversion

For electrocatalytic activity measurements in a PEMFC, CNF, or CNT were grown on carbon cloth (CC) by chemical vapor deposition (CVD) of ethane or propane, respectively. On the CC were deposited Ni particles by incipient wetness impregnation for the growth of CNF, or Fe/Co SBA-15 particles by dip-coating for the growth of CNT. Pt (20 wt %) was finally deposited on these nanoengineered carbon anodes by incipient wetness impregnation of a H_2PtCl_6 in $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$ (1 : 1 v/v) solution. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) measurements were made using a JEOL JMS 840 and a TOPCON EM-002B UHR or Philips TEM/STEM CM200 LaB6 apparatus, operating at 200 kV.

The PEM fuel cell anodes were then hot-pressed with Nafion® 112, used as proton exchange membrane, and with commercial Pt/carbon black (20 wt %) based gas diffusion electrode (GDE) from E-TEK, used as the cathode. Electrocatalytic activity in hydrogen oxidation was measured in a PEM fuel cell (geometric area 1 cm^2) working at r.t. and atmospheric pressure.

For electrocatalytic activity measurements in CO_2 conversion, the Pd nanoclusters were synthesized by stirring an acetic acid solution of Pd(II) acetate and bathophenanthroline disulfonic acid disodium salt in a molar ratio of 7 : 1 under H_2 until gas adsorption ceased (4 h) [10]. The brown-black solution was then exposed to O_2 flow to oxidize the free surface atoms. The Pt nanoclusters were prepared using LiBH_4 in tetrahydrofuran as the reducing agent and PtCl_2 in toluene in the presence of a surfactant DDAB (didecyldimethylammonium bromide). For the final preparation of the electrocatalyst, pieces of E-TEK ELAT carbon cloth were coated with a Nafion® SE-5112 suspension of the noble metal nanoclusters, cured at 180°C and then hot-pressed with a Nafion® 112 foil. The final amount of Pt electrocatalyst was 20 wt % in order to permit comparison with commercial 20 wt % Pt/C on carbon cloth (E-TEK).

Before the coating of E-TEK ELAT carbon cloth, the electrocatalysts were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM), using an ItalStructure APD 2000 diffractometer and a Philips CM 12 microscope, respectively.

2.2. Electrocatalytic Tests

Electrocatalytic activity measurements in hydrogen oxidation of the different electrocatalysts were carried out in a PEM fuel cell (geometric area 1 cm^2) working at room temperature and atmospheric pressure setting hydrogen and oxygen at a flow rate of 9 ml min^{-1} and 50 ml min^{-1} , respectively, and the characteristic polar-

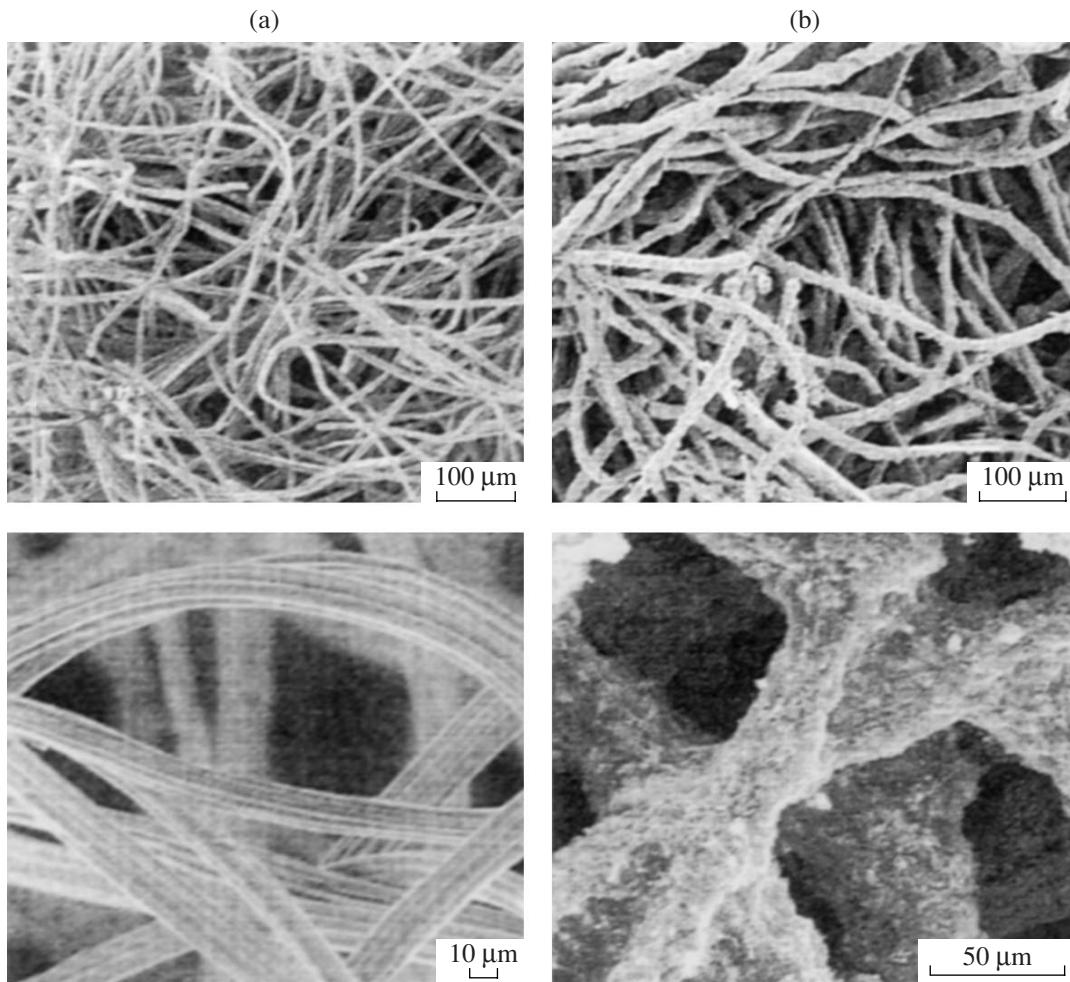


Fig. 1. SEM images of the microshaped carbon fibers support, carbon cloth (a) before and (b) after the synthesis of carbon nanofibers (CNFs).

ization curves V (cell potential) versus I (current density) were recorded connecting the two electrode electrochemical cell to a potentiostat/galvanostat (AMEL 2049).

Different MEAs (membrane and electrode assemblies) were prepared for electrochemical measurements using the different 20 wt % Pt/CNF-CC and 20% Pt/CNT-CC electrodes for the anode and always a commercial 20 wt % Pt/C on GDM electrode (E-TEK Inc.) for the cathode.

The electrocatalytic tests in the gas-phase CO_2 reduction were carried out in a reactor made of plexiglass divided into two parts and separated by the gas diffusion electrode (GDE) containing the different electrocatalysts. Before the reaction, the reactor was flushed under a continuous flow of N_2 and an applied current for 1 h in order to desorb all the impurities at the catalyst surface. Then, CO_2 was allowed to be adsorbed for 30 min. The catalytic tests were carried out under the following reaction parameters: flow of CO_2 = 20 cm^3/min , $[\text{KHCO}_3]$ = 0.5 mol/l, applied current

30 mA, 25°C, 1 atm. Experiments were conducted galvanostatically using a potentiostat/galvanostat (AMEL 2049). Analysis of the products was made using a gas-chromatograph (GC) equipped with an FID detector.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Nanostructured Electrocatalysts

The electrodes based on CNF and CNT are nano/micro composites, because the carbon nanofibers and the carbon nanotubes were grown by chemical vapor deposition on a microshaped carbon fiber support (cloth).

SEM images of the carbon cloth (Fig. 1a) show that the base carbon microfibers after the synthesis of CNFs were fully covered with a thick network of carbon nanofibers forming a layer of 3 μm around each one of the carbon microfibers, increasing their diameter by about 20% (Fig. 1b).

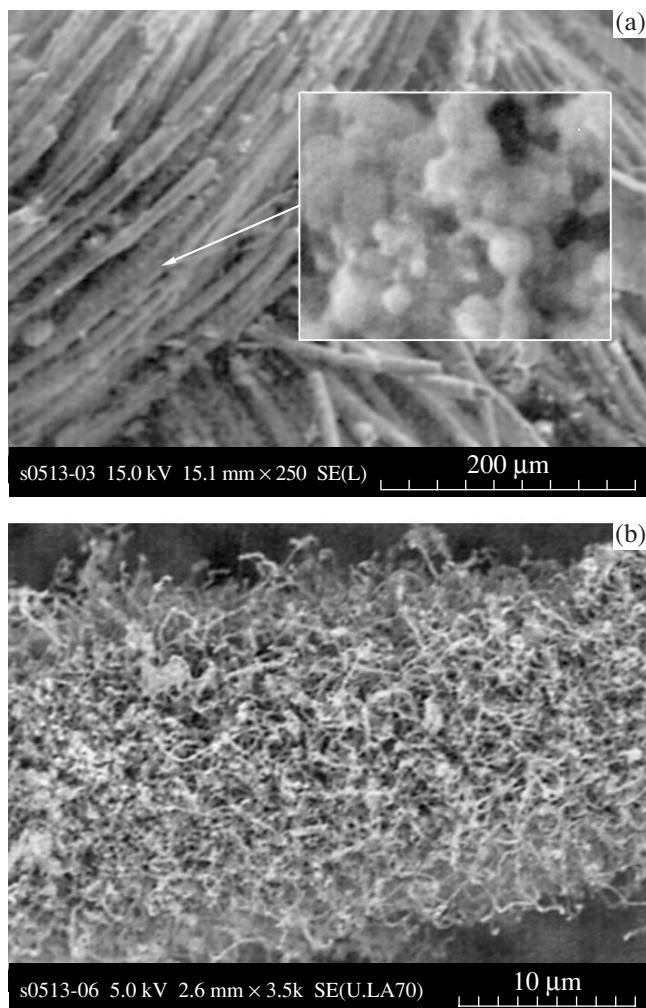


Fig. 2. SEM images of the FeCo/SBA-15/carbon cloth composite (a) before and (b) after CVD of propane.

SBA-15 was successfully synthesized directly on carbon cloth by the dip-coating method and allowed to disperse well Fe–Co bimetallic particles used as a cata-

lyst for the growing of carbon nanotubes (CNT) by chemical vapor deposition.

SEM characterization of the FeCo/SBA-15/carbon cloth composite clearly indicates the typical wreathlike morphology of SBA-15 (Fig. 2a) and evidences that a dense layer of carbon nanotubes is grown after CVD (Fig. 2b).

Before using CNT–CC and CNF–CC composites as the anode in a PEMFC, Pt (20 wt %) was deposited on the carbon nanoengineered anodes by incipient wetness impregnation.

TEM images (Fig. 3a) show that Pt particles have a mean diameter smaller than 2 nm and are dispersed mainly inside the carbon nanofibers grown on the microshaped carbon fibers support. Whereas, Pt particles are dispersed mainly on the external walls of carbon nanotubes with size distribution in the range 2–10 nm (Fig. 3b).

Pt nanoclusters–based electrocatalysts were characterized using X-ray diffraction and TEM analysis. Figure 4a reports the XRD patterns of Pt nanoclusters, and reflections correspond to metallic Pt. The broadening of the platinum d_{111} reflection indicates a mean diameter of the metal particles of about 2 nm. TEM investigations are displayed in Fig. 4b where good spherical-shaped particles are evident with a narrow distribution in the range 1–5 nm centered at 2 nm, which are in good agreement with XRD results.

3.2. Electrocatalytic Performance of Pt/CNF–CC and Pt/CNT–CC in PEM Fuel Cells

Generally, in PEMFCs, increasing the current density a decrease of cell potential is observed due to activation, ohmic, and concentration polarizations. The less pronounced this decrease, the better the fuel cell performance, because the maximum power density of the cell is higher. Then electrochemical characterization of Pt/CNF–CC and Pt/CNT–CC (20 wt %) is reported by the study of their V–I curves in comparison to

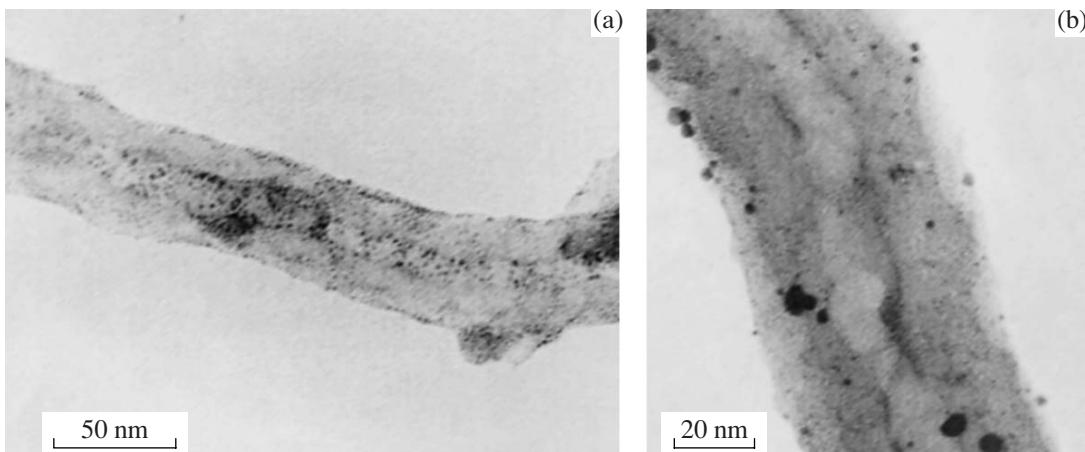


Fig. 3. TEM images of Pt nanoparticles deposited on (a) CNF and (b) CNT grown directly on carbon cloth.

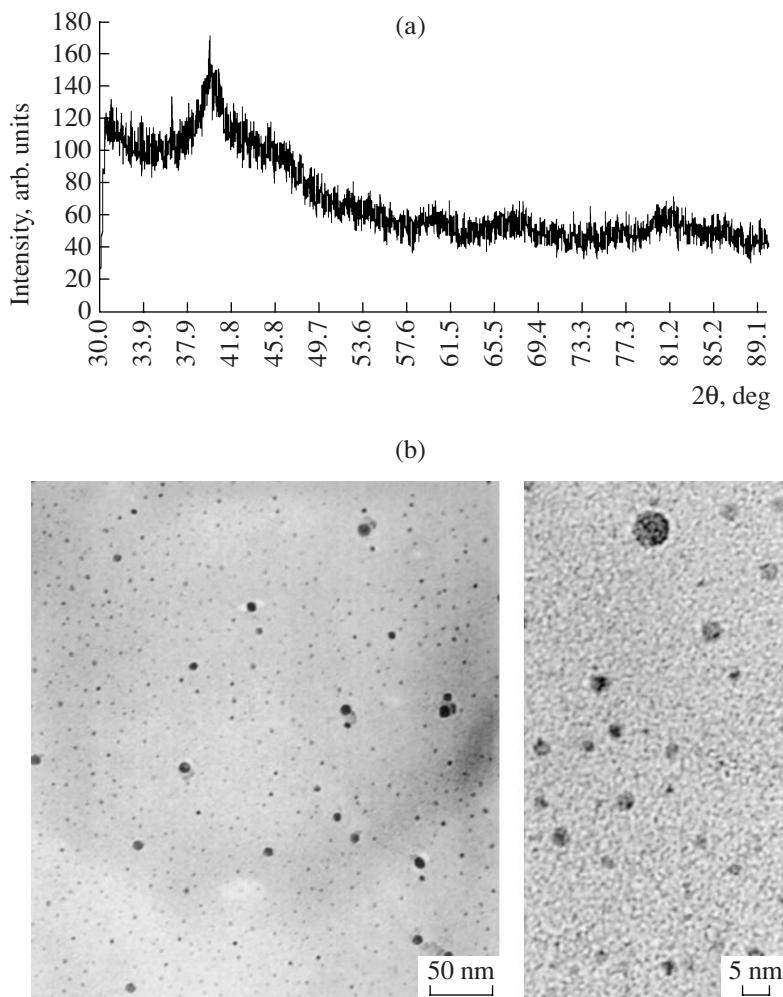


Fig. 4. (a) XRD pattern and (b) TEM image of the Pt nanoclusters used as the electrocatalyst in the GDE for CO_2 conversion.

a commercial Pt/carbon black catalyst from E-TEK Inc. used as reference and containing the same amount of Pt.

As can be observed in Figs. 5a and 5b, the electrocatalytic activity of the nanoengineered anodes with a hierarchically organized structure (Pt/CNF-CC and Pt/CNT-CC) is higher than that of the commercial Pt/carbon black anode. With respect to the commercial anode, both novel anodes show improved power density up to a current density of about 40 mA/cm^2 , but the Pt/CNT-CC deviates from this trend at higher current densities. The Pt/CNF-CC anode allows us to obtain a maximum power density about twice that of the commercial anode, with a consequent large increase in the efficiency in the chemical-to-electrical conversion efficiency. The physicochemical characterization of the samples, in particular by TEM and SEM, indicates that the effect should be attributed to the more efficient formation of the three-phase boundary. The loss of efficiency in the Pt/CNT-CC anode at high current density is instead related to mass transport losses, due to the confinement effect of H_2 inside carbon nanotubes,

whereas catalytic Pt particles are dispersed mainly on the external walls of CNT, as confirmed by TEM analysis. This electrochemical behavior is a trend presented by carbon nanostructures (Fig. 5a), less pronounced with the Pt/CNF-CC sample probably because the catalytic metal particles are dispersed mainly inside CNF where H_2 is confined too.

3.3. Electrocatalytic Performance of Pt and Pd Nanoclusters in CO_2 Conversion

The results of electrocatalytic CO_2 reduction after 30 min of application of a constant potential of 1.99 V to electrocatalysts based on Pt or Pd nanoclusters, deposited on the GDM and then hot-pressed with Nafion membrane, are reported in Fig. 6. The electrocatalytic behavior of a commercial 20% Pt/C-GDM-Nafion[®] catalyst is also reported for comparison.

After 30 min, the main products are $\text{C}_1\text{--C}_2$ hydrocarbons and alcohols for Pt nanoclusters, methanol, and also $\text{C}_1\text{--C}_3$ hydrocarbons for Pd nanoclusters; the reac-

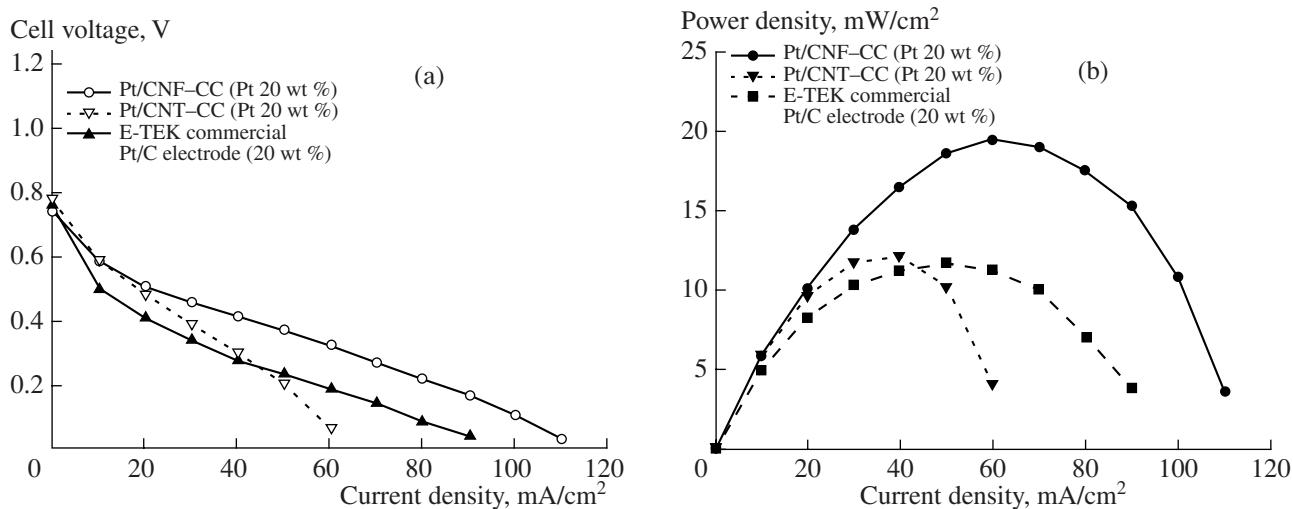


Fig. 5. Dependence of (a) cell voltage and (b) power density on current density for the different MEAs composed of the commercial E-TEK electrode (Pt/C 20 wt %) on both sides, Pt/CNF-CC and Pt/CNF-CC at the anode.

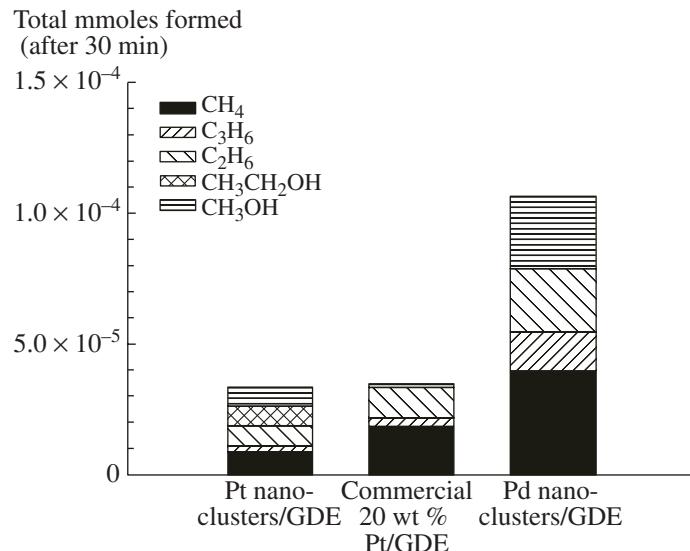


Fig. 6. Products from gas-phase electrocatalytic reduction of CO₂ over the different GDE-containing Pt nanoclusters, Pd nanoclusters, and commercial E-TEK Pt/C (metal loading 20 wt % for each one).

tion products increase with increasing time of bias application up to a maximum of about 30 min and then decrease due to the formation of heavier products which remain adsorbed on the GDM. The behavior of Pt nanoclusters is comparable to that of the commercial 20 wt % Pt/C electrocatalyst, but a marked change in selectivity was observed. In particular the formation of methane is strongly suppressed, while the formation of alcohols increased considerably.

The product profile is influenced by the nature of the active species. In particular, Pd nanoclusters show the highest productivity in hydrocarbons and alcohols.

The electrocatalytic results permitted us to hypothesize a Fisher-Tropsch-like mechanism of hydrocarbon formation.

4. CONCLUSIONS

The major observations drawn from the study on PEMFC are that the Pt/C interface is the dominant factor determining activation losses and the higher performance of nanostructured Pt–carbon anodes with respect to commercial one is considered to derive from the more efficient formation of the three-phase boundary. Also ohmic losses are the lowest due to the high

electrical conductivity of carbon nanostructures (CNT and CNF), but improvement of mass transport losses, which could be realized with the confinement of both H₂ and catalytic Pt particles inside CNT or CNF, is important for upgrading their electrocatalytic activity.

GDE based on Pt and Pd nanocluster electrocatalysts can be considered interesting materials for gas phase electrocatalytic reduction of CO₂ to fuels in photoelectrochemical devices which use solar energy to convert CO₂ back to fuels.

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