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Correlation of different carbon support and catalytic activity for Pt based catalyst

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Carbon supported platinum (Pt/C) constitute commonly used electrocatalysts in polymer electrolyte membrane fuel cells. For the catalyst preparation, Vulcan XC-72R is the most widely used as carbon support. Pt/C catalysts with different carbon supports are prepared by impregnation-reduction method using $NaBH_4$ as reductant. The carbon black, carbon aerogel and MWNts were used as Pt support. The electrochemical characteristics and the catalytic activity for oxygen reduction of the Pt based catalysts were evaluated and compared with commercial Pt/C from ETEK. In addition EDAX measurements were done to evaluate the final content of Pt:C, Pt:CA and Pt:MWNTs.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have drawn a great deal of attention in both fundamental and application in recent years [1]. Carbon-supported Pt or Pt-based alloys are the best electrocatalysts for the anodic and cathodic reactions in fuel cells [2]. One problem related to the development of PEMFCs is that the O_2 reduction proceeds at a very slow kinetic rate and the exchange current density of the oxygen reduction reaction at the Pt catalyst electrode is low compared with that for H_2 oxidation reaction [3-5].

Pt it is one of the main components of PEMFCs and water electrolyzers responsible for theirs efficiency and cost. As consequence of elevated price and limited resources, Pt cannot be used for large-scale applications and alternative materials are needed. Pt loading and particle size, as well as the nature of catalyst support, are important issues for the fabrication of efficiently electrodes for electrocatalysis reactions. For Pt catalyst reduction, two approaches are currently very active: exploration of non-noble catalysts and reduction of Pt loading [6]. Some promising approaches and results have been reported for Pt loading reduction through alloying or nano-particle supporting procedure. For MEA Pt loading reduction, the research has been focusing on improving the utilization of Pt through increasing the reactive surface area. Pt can be supported on some high-surface-area electronically conductive substrates such as carbon particles to form supported catalysts. Carbon black has been commonly used as catalyst supports in the PEMFCs for MEA preparation. Carbon nanotubes (CNTs) show great potential for improvement of fuel cell electrodes performances. They have a high surface area that can stabilize high Pt dispersions and can increase the electronic conductivity of the electrodes improving the gas transport rate through the electrodes reactive layers [7, 8].

In terms of catalyst supporting strategies, the most active area of the research is in CNTs supported Pt based catalysts, due to of higher electronic conductivities and high specific surface areas compared with Vulcan XC-72R, Black Pearls 2000, Ketjen Black, etc., commonly used as catalyst supports. The use of new forms of nanostructured carbon materials, such as CNTs, is the focus of considerable research [9-11].

Therefore, without sharply reducing Pt loading at both the cathode and anode, it is not likely to realize fuel cell commercialization [2]. It is very difficult to maintain or improve catalyst layer performance when the catalyst loading is reduced. In order to achieve that, the main purposes for using CNTs- and carbon aerogel (CA)-supported Pt catalysts are to reduce Pt loading through increasing the catalyst utilization, and improving the catalyst activity/performance. The main focus of this paper is the development of Pt/C catalysts with different carbon support prepared by impregnation-reduction method using $NaBH_4$ and Pt metal precursor. The carbon black (C), carbon aerogel (CA) and multi-wall carbon nanotubes (MWNTs) were used as Pt support. The electrochemical characteristics and the catalytic activity for oxygen reduction of the Pt based catalysts were evaluated and compared with commercial Pt/C from ETEK. In addition, EDAX measurements were done to evaluate the final content of Pt:C, Pt:CA and Pt:MWNT.

2. Experimental

The high surface-area Vulcan XC-72R (Cabot Co.) carbon was used as catalyst support for synthesis of Pt/C electrocatalyst.

The MWNTs used in this work were purchased from Shenzhen Nanotech PortoCo., Ltd., China (d<10 nm, length: 5-15 μm, P: ≥ 95%, specific surface area: 40-300 m^2/g). In order to improve the catalyst dispersion on their surface, the CNTs were chemical activated by refluxing with HNO_3 (3M) (Merck reagent) for 24 h, followed by washing with de-ionized water until neutral pH and dried in air for 60 min at 80^0C.

Carbon aerogels with of meso- and macro-porosity were obtained by sol-gel using a proprietary method presented elsewhere [12]. By polycondensation of resorcinol (R) and formaldehyde (F), wet resorcinol-formaldehyde (RF) gels were prepared. Using CO_2 supercritical drying, the RF gels were transformed into organic aerogels and to carbon aerogels by pyrolysis under nitrogen atmosphere. In this work, mesoporous carbon aerogels with high BET surface area of 860 m^2/g were used as catalyst support.

The Pt/C, Pt/MWNTs and Pt/CA catalysts were prepared by a conventional borohydride reduction method using $NaBH_4$ (15 mM) and H_2PtCl_6 (10%) – (Sigma-Aldrich products) as metal precursor. The composition of the prepared catalysts was determined by energy-dispersive X-ray analysis (EDAX) in a FEI-Quanta 400 scanning electron microscope provided with a microanalyser. The electrochemical measurements were carried out with a VoltaLab 40 potentiostat (PGZ301, RADIOMETER) using a conventional three-electrode electrochemical cell. Pt mesh and CR5/Hg_2S0_4 - MMS were used as the counter and reference electrode, respectively. The working electrode was 20% teflonised toray carbon paper sprayed with Pt/C, Pt/MWNTs or Pt/CA catalysts ink. The catalyst ink was prepared by sonicating the catalyst powder in isopropyl alcohol for 60 min. The cyclic voltammetry were carried out in a solution containing 0.5 M H_2SO_4 at room temperature.

3. Results and discussion

Results by EDAX analyses have indicated small discrepancies when compared with the nominal compositions expected from the relative amounts of precursors used in the preparation of the noble metal catalysts.

Table 1. Composition of prepared electrocatalytic systems identified by EDAX

Catalyst	Carbon (wt%)	Pt (wt%)	Oxygen (wt%)
Pt/C	60.33	38.82	0.85
Pt/MWNTs	77.25	21.52	1.22
Pt/CA	65.18	32.47	2.35

To characterize the basic electrochemical properties of the Pt/C, Pt/MWNTs and Pt/CA electrocatalysts the cyclic voltammmetry in sulfuric acid were performed. The solution is first degassed by bubbling nitrogen gas for about 30 min to record the background current–voltage curves. The cyclic voltammetry with well-defined peaks and linear sweep of Pt/C, Pt/MWNTs and Pt/CA in 0.5 M H_2SO_4 saturated with nitrogen and O_2, with a scan rate 5 mV/s are shown in Figs. 1-3.

Under these conditions, the voltammograms show the very well defined hydrogen adsorption–desorption region for all catalysts. How is observed, the reduction current increase in the case of solution saturated by oxygen being an indication of electrocatalytic activity towards oxygen reduction reaction (ORR).

In the case of Pt/C (Fig. 1) is observed a good activity towards ORR, with the limiting current two times higher for solution saturated with oxygen.

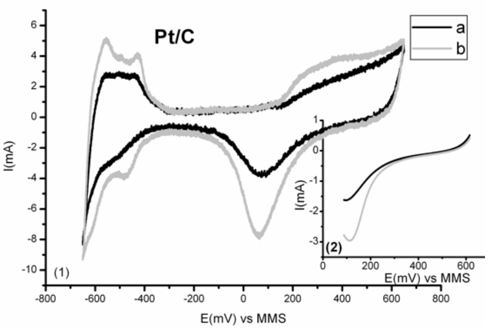

Fig. 1. Cyclic voltammetry with 20mV/s scan rate (1) and linear sweep with 5 mV/s scan rate (2) of Pt/C in 0.5 M H_2SO_4 saturated with nitrogen (black curve, a) and O_2 (grey curve, b).

Pt/MWNTs (Fig. 2) has a good electroactivity towards ORR, the oxygen reduction occurs at ca. 0.3 V. The limiting current of Pt/MWNTs in 0.5 M H_2SO_4 solution saturated with oxygen (b) is three times higher than in 0.5 M H_2SO_4 solution saturated with nitrogen (a). Also for Pt/CA is observed a good activity towards ORR, the limiting current is, in this case, ~1.4 times higher for solution saturated with oxygen.

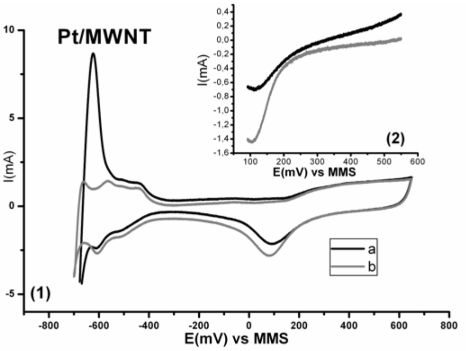

Fig. 2. Cyclic voltammetry with 20mV/s scan rate (1) and linear sweep with 5 mV/s scan rate (2) of Pt/MWNT in 0.5 M H_2SO_4 saturated with nitrogen (black curve- a) and O_2 (grey curve-b) .

The cyclic voltammograms of the Pt/C, Pt/MWNTs and Pt/CA catalysts in 0.5M H_2SO_4 solution are given in Fig. 4. Moreover, for the results presented in Fig.4 are taken in account the current density on Pt loading. Pt loading was calculated from total weight of catalyst and taking in account the EDAX results for each catalyst. It was found that (Fig. 4) the area of the hydrogen adsorption and desorption peaks for the Pt/CA catalyst are much larger than that for the Pt/C and Pt/MWNTs, according with the electrochemically active surface area of the catalyst.

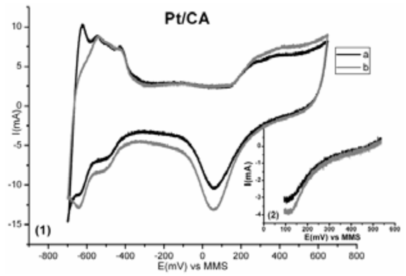

Fig. 3. Cyclic voltammetry with 20mV/s scane rate (1) and linear sweep with 5 mV/s scan rate (2) of Pt/CA in 0.5 M H_2SO_4 saturated with nitrogen (black curve- a) and O_2 (grey curve-b).

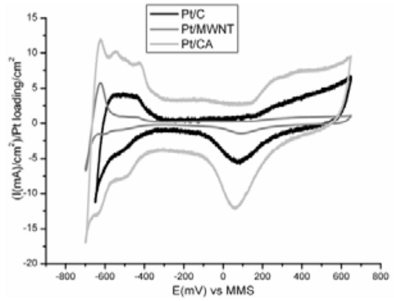

Fig. 4. Cyclic voltammograms of the Pt/C, Pt/MWNTs and Pt/CA catalyst electrodes in 0.5 M H_2SO_4 solution.

For a better comparison of electrocatalysts activity towards ORR, Fig. 5 displays the linear sweep voltammograms of oxygen at the Pt/C, Pt/MWNTs and Pt/CA catalyst electrodes in a 0.5 M H_2SO_4 solution. It is observed that the reduction potential of oxygen at Pt/C and Pt/CA catalyst electrodes is located at about 0.4 V and for Pt/MWNTs at 0.25 mV.

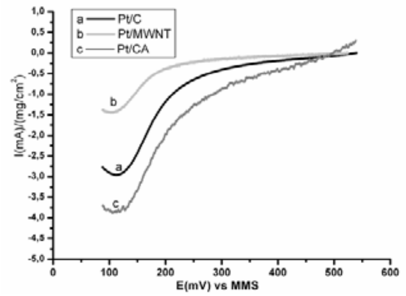

Fig. 5. Linear sweep with 5 mV/s scan rate of Pt/C –curve (a), Pt/MWNTs-curve (b) and Pt/CA- curve (c) in 0.5 M H_2SO_4 saturated O_2

From Fig. 5 it can be observed that Pt/CA gives the best activity towards ORR. The activity of Pt/MWNTs is lower than Pt/C and it is in concordance with EDAX results, were the quantity of Pt in the final composition was lower than that expected.

However, the limiting current density for the oxygen reduction at the Pt/CA catalyst electrode is higher than that for Pt/C and Pt/MWNTs electrodes, proving a higher electrocatalytic activity for oxygen reduction. This high electrocatalytic activity of Pt/CA catalysts for oxygen reduction can be attributed to their high electrochemically active area.

4. Conclusions

The above results illustrate that the Pt/CA catalysts prepared by the borohydride reduction method showed the best electrocatalytic activity for the oxygen reduction compared with the Pt/C or Pt/MWNTs obtained by the same method. Therefore, the results of the linear sweep voltammetry indicate that the limiting current density for the oxygen reduction at the Pt/CA catalyst electrode is better than that for Pt/C or Pt/MWNTs catalyst electrode. Based on above results, we can conclude that the use of another catalyst supports as MWNTs and carbon aerogel is a good alternative to reduce catalyst loading through increasing the catalyst utilization, and improving the catalyst activity performance.

Acknowledgments

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