

New Metallic Electrocatalysts Prepared by Galvanostatic Pulse Electrodeposition. Application to the Direct Methanol Fuel Cell (DMFC)

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Introduction

One of the key point to develop a DMFC is to investigate new electrocatalysts for the oxidation of methanol at the anode, allowing to increase the current density and to decrease the anodic overvoltage [1]. Several studies in the 3 past decades have shown that the best electrocatalyst for methanol oxidation is a platinum-ruthenium system, although the optimum composition was not ascertained with accuracy [2].

For practical anodes of a DMFC based on a Proton Exchange Methanol Fuel Cell (PEMFC), the electrocatalyst is deposited on a carbon black powder (usually Vulcan XC-72) by chemical reduction of platinum and ruthenium salts. Then a mixture of the Pt/Ru/C electrocatalyst with a PTFE suspension, and eventually with a Nafion® solution is deposited by rolling and/or by brushing process on a carbon cloth or a carbon paper, carrying a carbon powder diffusion layer [3]. These methods of preparation give usually relatively thick electrode layers (10 to 50 μm), which leads to increase the diffusion overvoltage due to transfer of the reactants towards the catalytic sites.

One way to prepare electrocatalysts with a lower precious metal loading and an higher availability of the reactants to the catalytic sites is to depose directly the catalyst into the porous structure electrode by electrochemical methods. In such a way the utilization of the electrocatalyst is much greater since the electrochemical reaction occurs only at the interface of the membrane and the electrode. Usually metal electrodeposition is better carried out by pulse techniques, preferably galvanostatic pulses [4]. These authors showed that efficient platinum catalytic layers can be prepared for a H_2/O_2 PEMFC.

Until now only pure platinum electrocatalysts were prepared by electrodeposition. Therefore the aim of this communication is to investigate a new way of preparing Pt-Ru electrocatalysts of different composition and to determine their activity for methanol oxidation in a DMFC.

Experimental

Gas diffusion electrodes were prepared using a carbon cloth as a support for the gas diffusion layer consisting of a mixture of Vulcan XC72 carbon powder and PTFE dissolved in isopropanol.

Electrodeposition of Pt-Ru alloys, from a solution containing K_2PtCl_6 and K_2RuCl_5 in the desired ratio, was realized in a 2 compartment cell using a high power potentiostat (Wenking HP88) and an arbitrary waveform generator (HP33120A). Different current density vs. time programs were used, with pulse times ranging from 10 to

500 ms, and relaxation times from 1 to 10 s. Current densities were chosen in the range 10-100 mA cm^{-2} .

The electrode structure and composition were determined by XRD analysis and TEM observation coupled with EDX analysis.

Prior to their use in the fuel cell, the electrodes were covered with a thin layer of a mixture of water and Nafion® solution in alcohol (Aldrich). Then the membrane electrode assemblies (MEA) were prepared by hot pressing this electrode on a Nafion®117 membrane, together with a cathode from E-TEK containing 2.0 mg Pt cm^{-2} .

The electrical characteristics (E-j and P-j curves) were determined using a Globe Tech Fuel Cell station specially equipped with a piston pump allowing the circulation of a methanol/water mixture in the anodic compartment. The temperature of the DMFC was varied from 50°C to 110°C.

Results and Discussion

a) Electrode preparation and characterization

Several electrodes with different Pt-Ru (1/1, 2/1 and 4/1) ratios were prepared containing 2 mg cm^{-2} of the electrocatalysts.

The XRD patterns showed that most electrodes (2/1 and 4/1 Pt/Ru ratios) consist of a Pt-Ru alloy with the desired composition, as confirmed by EDX analysis.

Observation of the electrode surface by TEM and fit of the XRD patterns lead to the conclusion that the Pt-Ru particles are relatively well dispersed with an average size from 5 to 8 nm.

b) Fuel cell tests

The cell voltage E(j) and the power density P(j) vs. current density j curves were recorded at different working temperatures (50, 70, 90, 100 and 110°C) for a single DMFC fed with pure oxygen (pressure between 1.4 and 2.5 bar) on the cathode side and 2 M CH_3OH in pure water on the anode side (pressure between 1.2 and 2.0 bar). The maximum power density increases from 35 mW cm^{-2} for the lowest temperature (50°C) with a 1/1 Pt-Ru anode to 85 mW cm^{-2} at 110°C for the best electrocatalyst (4/1 Pt-Ru anode).

These results recorded in a working DMFC prove again that the best Pt-Ru electrocatalyst consists of a $\text{Pt}_{0.8}\text{Ru}_{0.2}$ alloy highly dispersed on a gas diffusion carbon electrode. This is in perfect agreement with half cell studies, showing that 4 Pt sites together with 1 Ru site are necessary to accommodate the methanol electrooxidation reaction [5].

References

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