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Characterization of the electrocatalytic activity of carbon-supported platinum-based catalysts by thermal gravimetric analysis

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Investigations of carbon-supported Pt, Pt_3Co, and Pt_3Ni electrocatalysts using thermal gravimetric analysis (TGA) in combination with electrochemical measurements of the membrane electrode assemblies (MEA) for proton exchange membrane fuel cells have demonstrated that the onset temperature of the carbon support thermal oxidation and apparent activation energy of this reaction decrease in the following orders: Pt(20%)/C > Pt(35%)/C > Pt(46%)/C and Pt_3Ni/C > Pt_3Co/C > Pt/C, while MEA power density increases. Thus, TGA can be used as a simple and express technique for analysis of the electrocatalytic activity of carbon-supported Pt-based catalysts for proton exchange membrane fuel cells.

Carbon-supported platinum (Pt/C) is the best known electrocatalyst for both hydrogen oxidation and oxygen reduction in proton exchange membrane fuel cells (PEMFCs).[1] However, it is important to develop new inexpensive catalysts with improved catalytic activities.[1] There are several strategies aimed at improving the performance of nanostructured catalysts, such as the formation of catalysts with different compositions[2,3] and different active component morphologies.[4]

Currently, two basic electrochemical approaches are commonly used for the investigation of the catalytic activity of Pt catalysts: (i) polarization measurements on a stationary or rotating disk electrode and (ii) measurements of membrane electrode assemblies (MEA). However, these methods are time-consuming and labor-intensive.

X-ray diffraction is used for the evaluation of both structural (unit cell) and microstructural Pt/C parameters, such as average particle size, grain size distribution, and nanoparticle shape.[5] The catalytic activity strongly depends on the above characteristics.[6]

Carbon black undergoes electrochemical oxidation to surface oxides, which are converted to CO_2 at the electrodes of a fuel cell. The presence of Pt significantly accelerates the rate of carbon corrosion[7] and decreases the thermal stability of carbon supports.[8] A correlation between the shape of the TG/DTG curves and the fraction of carbon microparticles, which were poorly coated with platinum, can be used to analyze the uniformity of the Pt nanoparticle spatial distribution in metal–carbon catalysts.[9] Thus, an interesting aspect of these studies is the possibility of using the oxidation of carbon by O_2 as a versatile reaction probe to obtain information on the electrocatalytic activity of carbon-supported Pt catalysts. This knowledge may simplify and accelerate electrode material tests for PEMFCs.

Two series of catalysts were prepared and analyzed:[†] (I) Pt/C with 20, 35 and 46% Pt and (II) catalysts with pure platinum and its alloys with nickel Pt_3Ni and cobalt Pt_3Co containing 20% platinum. The remaining mass fractions (for all of the as-prepared materials that were studied using TG and EDAX analysis) were close to the theoretical metal loadings that were determined by the mass loss of the electrodes during the electrochemical synthesis of the catalysts (Table S1[‡]).

The XRD pattern of the synthesized Pt/C catalyst corresponds to the Pt face-centered cubic structure of platinum (Figure S1[‡]). For the Pt_3Ni and Pt_3Co particles, the diffraction peaks are shifted to higher angles compared with the peaks of pure Pt nanoparticles of the same size. This suggests that the synthesis leads to the formation of alloyed nanoparticles. An average particle size of 9±1 nm along the <111> direction (D111) was calculated using the Scherrer equation[10] for all of the samples. The TEM images showed that

[†] The preparation of the Pt/C, Pt_3Co/C and Pt_3Ni/C catalysts was performed *via* the electrochemical dispersion of metals using a pulse alternating current technique.[2,3,5] Carbon black Vulcan XC-72 (Cabot Corp., Boston, USA) was used as a support.

The XRD studies were performed on the Swiss-Norwegian beam lines at the European Synchrotron Radiation Facility (SNBL ESRF) using monochromated radiation (λ = 0.72287 Å) and a Mar-345 Image Plate detector.

The Raman measurements were performed at room temperature using an inVia Reflex Renishaw micro-Raman system in the backscattering configuration. The samples were excited with an Ar laser at a wavelength of 488 nm, and the spectra were collected using a microscope with a 100× magnification.

The TEM images of the catalysts were obtained on a Carl Zeiss LEO 912 AB microscope. Energy dispersive X-ray microanalysis (EDAX) was conducted using EDX Zeiss LEO SUPRS 25. The thermogravimetric analysis was performed on a Mettler-Toledo TGA/DSC 1 thermal analyzer using the STAR System software for data processing. The sample (approximately 50 mg) was heated from 308 to 1273 K at heating rates of 5, 10 and 15 K min^{-1} under a purified air (flow rate of 30 cm^3 min^{-1}).

The fuel cell tests of the materials were performed for the MEA with a 1 cm^2 geometric area of the electrodes using a P-150 potentiostat (Elins) in an oxygen/hydrogen system (wetting 100%, 297 K). The MEA, in which the anode and cathode contained the synthesized catalyst with a metal loading of 0.4 mg_{Pt} cm^{-2}, was manufactured on a Nafion®212 membrane using an airbrushing method.[2]

[‡] See Online Supplementary Materials.

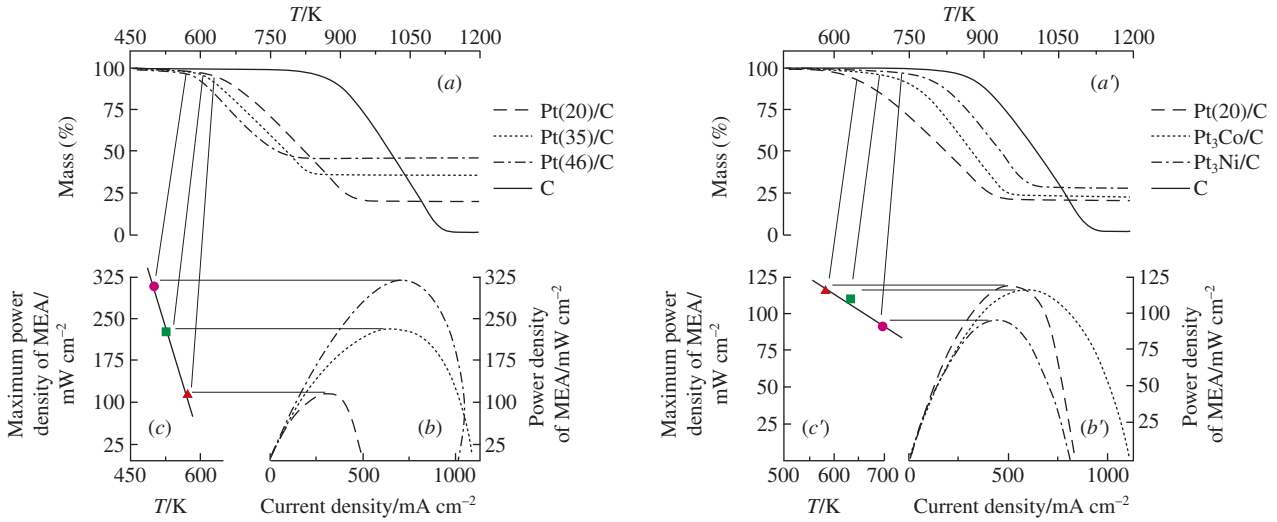

Figure 1 A comparison of the data from the TGA and MEA measurements: (*a*) TG curves of Vulcan XC-72 and synthesized Pt(20%)/C, Pt(35%)/C and Pt(46%)/C and (*a'*) Pt_3Ni/C, Pt_3Co/C and Pt/C catalysts with the same 20% platinum loading (β = 10 K min^{-1}); (*b*) and (*b'*) power density curves recorded in MEA with different catalysts at 297 K; (*c*) and (*c'*) correlation between max power density of MEA and T_{onset} of thermal oxidation of the carbon support.

the metal nanoparticles are uniformly distributed over the surface of the carbon support and partially agglomerated (Figure S2‡).

The mass loss (TG) curves measured during the combustion (in air) of the Vulcan XC-72 and the synthesized materials are shown in Figure 1. The TG curves of the Pt/C with different Pt loading samples (I series) and alloy catalysts (II series) reveal a significant decrease in the carbon oxidation temperatures, T_{onset}, compared with the non-decorated Vulcan XC-72. The T_{onset} decreases in the following orders: Pt(20)/C > Pt(35)/C > Pt(46)/C and Pt_3Ni/C > Pt_3Co/C > Pt(20)/C.

The polarization and power density measurements of the symmetrical MEA for the PEMFC that employed the as-prepared catalysts as anode and cathode catalysts exhibited a power density increase in the following orders: Pt(20)/C < Pt(35)/C < Pt(46)/C and Pt_3Ni/C < Pt_3Co/C < Pt(20)/C [Figure 1(*b*),(*b'*) and Table S1‡].

A comparison of the data from the TGA and MEA measurements shows that, as the electrocatalytic activity of the catalysts increases, the T_{onset} of the carbon support oxidation linearly decreases for both series of the as-prepared materials [Figure 1(*c*),(*c'*)]. The catalytic activity of the prepared catalysts correlates not only with the T_{onset} but also with the apparent activation energy of the thermal oxidation of carbon support, which decreased similarly to the T_{onset} (Figures S3, S5‡).

The transition metal nanoparticles may deform the carbon surface and cause local defects to form on the surface that could enhance the chemical reactivity and reduce the oxidation temperature and the gasification of the carbon.[8] To verify this assumption, we investigated three samples of Vulcan XC-72 (as-obtained, preliminarily treated with NaOH and decorated with Pt nanoparticles) using Raman spectroscopy.‡ The treatment of Vulcan XC-72 with NaOH increased its structural order, which was accompanied by a decrease in the number of defects at the surface of the sample after the thermal treatment (Figure S6‡). However, for the platinized Vulcan XC-72, the defect concentration at the surface of the graphite layer increased, but this growth is not sufficient to explain the substantial reduction of the apparent activation energy.‡,[11]

One possible explanation of the fact that the carbon support decorated with Pt nanoparticles oxidized more rapidly than by using O_2 from the gas phase is the spill-over effect.[12] In this case, the catalytic effect of the metal particle partially depends on the thermodynamics of oxidation and thus varies from one element to another, suggesting a possible reason for the differences between the observed catalytic effects of the metals on the carbon (Figure S7‡).

The carbon-supported Pt, Pt_3Co, and Pt_3Ni electrocatalysts were studied by TGA in combination with electrochemical measurements. The MEA tests indicate that the catalytic activity rises in the orders Pt_3Ni/C < Pt_3Co/C < Pt/C (with the same 20% platinum loading) and Pt(20%)/C < Pt(35%)/C < Pt(46%)/C. Additionally, the thermogravimetric data suggest that both the T_{onset} of thermal oxidation of the carbon support and the apparent activation energy of this reaction diminish with growing catalytic activity.

Thus, based on the results, we consider TGA to be a versatile reaction probe for the extraction of preliminary information on the electrocatalytic activity of carbon-supported Pt-based catalysts prepared using the same method.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2015.11.024.

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