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High low-temperature CO oxidation activity of platinum oxide prepared by magnetron sputtering

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ABSTRACT

CO oxidation on platinum oxide deposited by magnetron sputtering on flat (Si) and highly porous (multi-walled carbon nanotubes, MWCNT) substrates were examined using X-ray photoelectron spectroscopy, scanning tunneling microscopy, temperature-programmed desorption and temperature-programmed reaction in both UHV and ambient pressure conditions. Platinum in the freshly deposited thin film is present entirely in the 4+ oxidation state. The intrinsic CO oxidation capability of such catalyst proved to be significantly higher under approx. 480 K than that of pure platinum, presumably due to the interplay between metallic and cationic platinum entities, and the reaction yield can be further enhanced by increasing effective surface area when MWCNT is used as a support. The thermo-chemical stability of the platinum oxide, however, has its limitations as the thin film can be gradually thermally reduced to metallic platinum (with small residuum of stable Pt^{2+} species) and this process is further facilitated in the presence of reducing CO atmosphere.

1. Introduction

Besides other applications such as dielectric or ferroelectric films for micro- and nano-electronics, or optical materials, platinum and its oxides have been commonly used as a catalyst in chemical and electrochemical applications. In proton exchange membrane fuel cells (PEMFC) highly dispersed platinum is often used as a chemically active material incorporated into one or both fuel cell electrodes. It has been speculated that due to oxidizing environment during fuel cell operation the platinum may exist in the form of an oxide rather than metal. Since active catalytic material such as platinum is (both in practical applications and model studies) often deposited on an oxide support, the oxygen can also be diffusively interchanged with the substrate. In particular, this phenomenon can be expected on the commonly used cerium oxide (ceria), which exhibits quite unique properties attributed to its high oxygen storage capacity [1]. Thus ceria acts as an oxygen buffer which can be easily reduced and re-oxidized [2], readily changing ionization or oxidation state of the adsorbed species or layers and/or inducing a local charge transfer.

Since the reactivity of metallic and oxidic form of platinum is generally different [3,4], the performance of a Pt-based fuel cell may be sensitive to the oxidation state of platinum or the presence of oxygen within the catalyst volume. One of the reactions determining performance and lifetime of hydrogen- or methanol-fueled PEMFC is oxidation of CO, commonly present in hydrogen produced by hydrocarbon reforming (in hydrogen-fueled FCs) or being a by-product of methanol reforming (in methanol-fueled FCs), respectively.

Several types of platinum oxides have been reported so far. Pure crystalline compounds, including tetragonal PtO [5–9], cubic Pt_3O_4 [9,10], Pt_5O_6 [10,11], Pt_3O_8 [10], and PtO_2 [9] where the latter exists in two crystal modifications – α-PtO_2 [7,8] with hexagonal structure and orthorhombic β-PtO_2 [10,12,13]. Non-stoichiometric amorphous phases of platinum oxide (α-PtO_x) have also been prepared [14–17].

As a noble metal, platinum is relatively difficult to be bulk oxidized directly. Oxidation process can be, however, facilitated by electrochemical means or by reactive sputtering, where either oxygen plasma induces formation of an oxide film on a pristine platinum surface [18] or the platinum is sputtered away from a target in a mixture of oxygen and a noble gas (usually argon) using magnetron and deposited onto a solid substrate; in this technique the resulting composition of the oxide is determined by the deposition rate, the gas composition and pressure, and substrate temperature [7,15,19].

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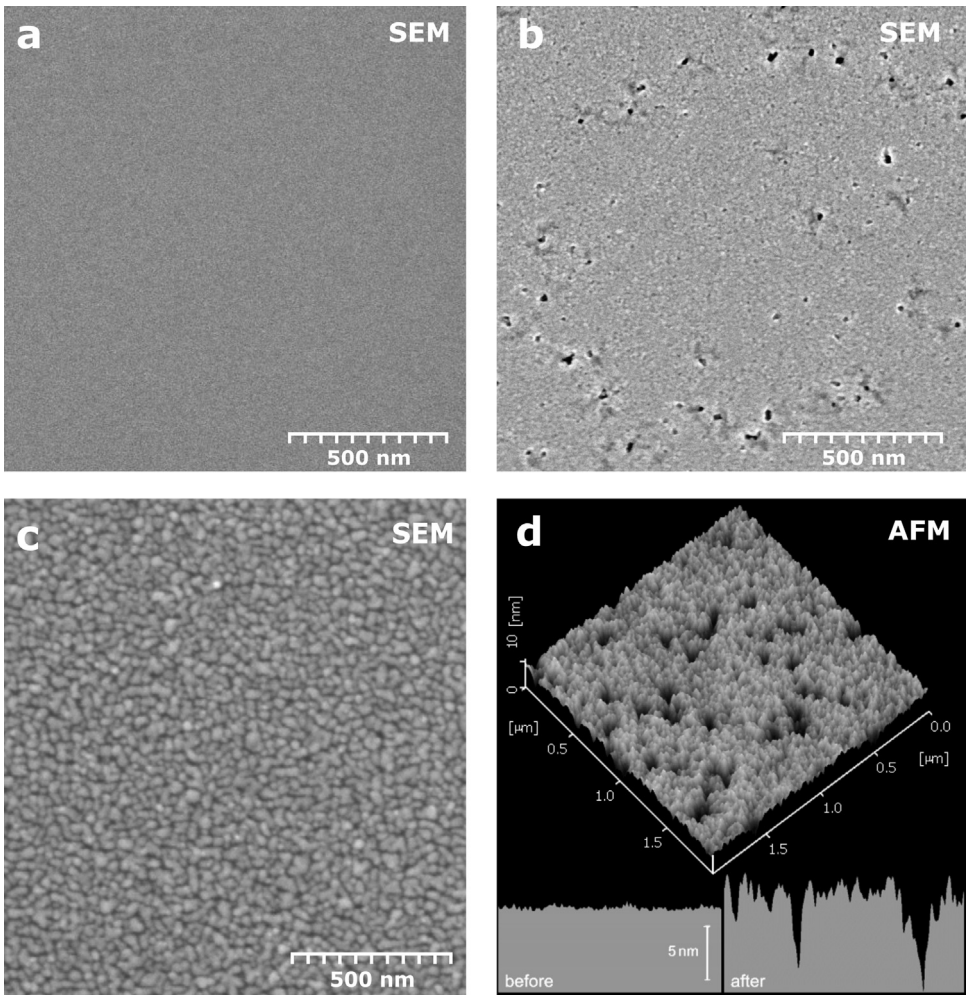

Fig. 1. SEM images (1500 nm × 1500 nm) of PtO_x/Si (a) as deposited, (b) annealed to 575 K in vacuum, (c) after high-pressure CO oxidation reaction in reactor (see text for details); (d) AFM image (2 μm × 2 μm) of the same surface as in (b); typical height profiles of the PtO_x layer before (left) and after (right) the heating are shown at the bottom.

2. Experimental

Samples of platinum oxide thin films supported on various substrates (multi-walled carbon nanotubes (MWCNTs) supported on Si(1 1 1) wafer, oxidized Si(1 1 1), and Ta polycrystalline foil) were prepared using reactive DC magnetron sputtering from a Pt target (99.95%) in pure oxygen atmosphere (Linde Gas, purity 5.6). Deposition was carried out with substrates at room temperature and 4×10^{-1} Pa pressure of O_2. We used Advanced Energy MDX500 power supply in power regulating mode, the applied power was 15 W yielding discharge voltage of about 480 V. The samples were placed 90 mm away from the 2″-diameter target. At these conditions the average deposition rate of 3 nm/min was achieved. In every run more substrates of the same type were placed in the magnetron simultaneously in order to produce a set of identical samples to be subjected to different experimental procedures.

The surface morphology of the samples was imaged by means of scanning electron microscopy (SEM; TESCAN-MIRA microscope) operated at 30 keV of primary electron beam energy.

X-ray photoelectron spectroscopy (XPS) was performed with an Al X-ray source ($h\nu$ = 1486.6 eV, energy resolution ΔE = 1 eV) and the SPECS Phoibos MDC 9 energy analyzer. All the XPS experiments were done in an ultrahigh vacuum (UHV) experimental chamber operating at base pressure <10^{-7} Pa.

The reactivity tests at atmospheric pressure were done using a home-made microchip reactor system. The gas composition is mixed using digital mass flow controllers, analysis of the gas composition is done by a Pfeiffer Prisma 200 series quadrupole mass spectrometer placed in a UHV chamber into which a small part of the product gas mixture is sampled through a metering leak valve. For CO oxidation experiments a $CO + O_2$ mixture (3 sccm CO + 7 sccm O_2) was diluted in an inert buffer gas (He, 30 sccm) to form a total pressure of 1 atmosphere inside the reactor. The design of the microreactor is specific in that the reaction chamber is formed by a flat sample at the bottom and a quartz glass cover with gas feeding holes and channels for better distribution of the gas flow at the top. The space between the two plates is retained by a 100 μm thick silicone rubber sealing placed around the sample circumference. Heating of the sample is computer controlled using a PID regulator.

The temperature-programmed desorption (TPD) and low-pressure temperature-programmed reaction (TPR) experiments were performed in another UHV system (<10^{-8} Pa base pressure) equipped with Pfeiffer PrismaPlus quadrupole mass spectrometer placed in a differentially pumped nozzle in order to separate background contribution from the molecules desorbing directly from the sample. In this apparatus the platinum oxide surface was exposed by pure carbon monoxide via a simple collimated gas dosers aimed directly at the sample surface. The samples were inserted into the UHV chamber immediately after the oxide deposition and used in experiments without any prior treatment.