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A more active Pt/carbon DMFC catalyst by simple reversal of the mixing sequence in preparation

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Abstract

Vulcan XC-72 carbon-supported Pt nanoparticles are prepared by a conventional route, i.e. by adding $NaBH_4$ solution to a carbon slurry of a Pt precursor salt (Pt-1/C); and by a simple reversal of the mixing sequence in which the Pt precursor salt was added to a carbon slurry of $NaBH_4$ (Pt-2/C). Transmission electron microscopy and X-ray photoelectron spectroscopy are used to obtain information on the particle size and size distribution, as well as on the surface oxidation state of the Pt nanoparticles. From cyclic and anodic CO-stripping voltammetric evaluation of catalyst activity for the methanol oxidation reaction (MOR) in acidic solution at room temperature, the Pt-2/C catalyst, which has none of the attributes generally associated with a good Pt catalyst (small particle size, narrow size-distribution, high metal dispersion, low Pt oxidation state), demonstrated higher specific activity and improved CO tolerance than the conventionally prepared Pt-1/C, which has all the common features of a good Pt catalyst. It is concluded that the higher activity of Pt-2/C is linked to its surface oxygen species, which is present in greater abundance and in a more accessible form for reaction with the strongly adsorbed CO-like intermediates.

Keywords: Platinum nanoparticles; Methanol oxidation reaction; CO tolerance; Specific activity; Catalyst; Carbon slurry

1. Introduction

The catalytic electro-oxidation of methanol at room temperature is the principal feature of direct methanol fuel cells (DMFCs), which are well poised to become the fastest growing next-generation mobile power source [1]. The catalysts used are invariably Pt based and rendering the Pt into a highly active form is an important design consideration. Despite ongoing debates on the optimum size of the Pt particles and the role of metal–support interactions, it is generally believed that a good carbon-supported Pt catalyst should have some predetermined features such as small particle size, narrow particle size distribution, a high state of dispersion on the support, and Pt in the fully-reduced metallic state. This study presents data contrary to these selection criteria.

Many methods have been reported for the preparation of carbon-supported Pt catalysts, among which the chemical reduction of Pt precursors is probably the most common. The conventional route to the formation of Pt particles is to introduce the reducing agent dropwise to a Pt precursor solution, or a carbon slurry of the Pt precursor solution [2–4]. Reasonably good control of particle size, particle size-distribution and the state of dispersion on the carbon support can often be accomplished by this simple technique [5]. In this work, an unusual route to Pt formation route has been deliberately adopted, namely, addition of the Pt precursor solution to a carbon slurry of the reducing agent $NaBH_4$. The resulting carbon-supported Pt catalyst has a broader particle size-distribution, a less-than-uniform metal dispersion, and a higher content of oxidized Pt on the particle surface. Despite these features, the catalyst has performed well for temperature methanol oxidation at room temperature, in terms of catalyst specific activity and CO tolerance.

2. Experimental

Chloroplatinic acid (H_2PtCl_6) was purchased from Aldrich. Sodium borohydride ($NaBH_4$), sulfuric acid (95–97%) and methanol were supplied by Merck. The carbon support was

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Vulcan XC-72 (measured BET surface area of 228 $m^2 g^{-1}$ and average particle size of 40–50 nm) from Cabot. All chemicals were used as received without further purification. De-ionized water was employed throughout the study.

Two Pt catalysts were prepared on Vulcan XC-72 carbon at a 20 wt.% of metal loading.

(1) Pt-1/C ('control'): 2 ml 50 mM H_2PtCl_6 was mixed with 120 ml of de-ionized water that contained a calculated amount of Vulcan XC-72 carbon, followed by 30 min of sonication. A 2 ml sample of a solution containing 100 mg $NaBH_4$ was added dropwise to the carbon suspension with vigorous stirring at room temperature. Stirring was continued overnight before the solid phase was recovered by filtration and then washed copiously with water. The recovered solid was dried under vacuum at room temperature overnight.
(2) Pt-2/C: 120 ml of de-ionized water containing a calculated amount of Vulcan XC-72 carbon was sonicated for 30 min in an ultrasonic bath to form a carbon slurry. Hundred milligrams of $NaBH_4$ was immediately added together with 2 ml of 50 mM H_2PtCl_6. The rest of the preparative procedures were the same as those used for the preparation of Pt-1/C.

X-ray powder diffraction (XRD) patterns of the catalysts were recorded with a Rigaku D/Max-3B diffractometer (Shimadzu) that used Cu Kα radiation ($\lambda = 1.5406$ Å). The 2θ angles were scanned from 20° to 85° at 2° min^{-1}. The diffraction data was curve-fitted by a least-squares program that was provided by the equipment manufacturer. Elemental compositions, of the Pt loading in particular, were determined by an EDX analyzer attached to a JEOL MP5600LV scanning electron microscope (SEM) that operated at 15 kV. Information on particle size, shape and size distribution was obtained with a JEOL JEM2010 transmission electron microscope (TEM) at 200 kV. X-ray photoelectron spectra were obtained from an ESCALAB MKII spectrometer (VG Scientific) using Al Kα radiation (1486.71 eV). Spectral correction was based on the graphite C1s level at 284.5 eV. The vendor-supplied XPSPEAK version 4.1 was used to deconvolute the XPS data; fixed half widths and fixed spin orbit splitting were used in the first trials.

An Autolab PGSTAT12 potentiostat/galvansotat, and a standard three-electrode electrochemical cell were used to evaluate the catalysts by cyclic voltammetry. The working electrode was a vitreous, glassy-carbon disc electrode (5 mm diameter) that was cast with a catalyst ink in Nafion solution to a Pt loading of 18 $\mu g\, cm^{-2}$. A Pt gauze and a saturated calomel electrode (SCE) were used, respectively, as the counter electrode and the reference electrode to complete the circuit. The electrolytes were 0.5 M H_2SO_4 and 1 M CH_3OH in 0.5 M H_2SO_4. A potential window of −0.2 to 1 V (with respect to SCE) was scanned at 20 $mV\, s^{-1}$ until a stable response was obtained before the voltammograms were recorded. The CO tolerance of the catalysts was evaluated by anodic stripping of adsorbed CO. This was done by saturating 0.5 M H_2SO_4 with 10% CO in Ar while the working electrode was held at −0.15 V for 30 min. The passage of CO was then stopped and the electrolyte was thoroughly purged with high purity Ar. The CO-stripping voltammograms were collected over the −0.2 to 1 V potential window starting from −0.15 V.

3. Results and discussion

The Pt loadings in Pt-1/C and Pt-2/C were about 20 wt.% as determined by EDX. Transmission election micrographs and the corresponding particle size-distributions of the two catalysts (Pt-1/C and Pt-2/C) are shown in Fig. 1. The Pt particles in Pt-1/C had a number-averaged particle size of 4.1 nm ($\sigma = 1.7$ nm) and were fairly uniformly distributed on the carbon support (Fig. 1(a)). By contrast, the Pt particles in Pt-2/C followed a bimodal distribution, with a mean of 5 nm for the larger particles and a mean of 0.8 nm for the smaller ones. Isolated Pt nanoparticles can also be found outside the carbon support, which is not the case with Pt-1/C. Low magnification TEM images (data not shown) of Pt-2/C also showed a few XC-72 flakes to be completely devoid of Pt. The difference between the two catalysts can be understood in terms of a series reaction scheme in which particle nucleation and growth are consecutive reactions with large particles as the final product. In the preparation of Pt-1/C, the addition of $NaBH_4$ to $PtCl_6^{2-}$ creates heterogeneity in the Pt source concentration (reacted versus un-reacted) which favours the formation of the end product [6]. Nucleation probably occurs preferentially on the carbon support by the reaction between adsorbed $PtCl_6^{2-}$ anions and incoming reducing agent $NaBH_4$ [7]. Further addition of $NaBH_4$ results in $PtCl_6^{2-}$ reduction and particle growth because the creation of new nuclei is not energetically favourable in the solution phase. In the case of Pt-2/C, where $PtCl_6^{2-}$ is the limiting reactant among an excess of $NaBH_4$, nucleation has to be initiated in the solution phase, and the Pt particles formed are subsequently deposited on the carbon support. Since the particles are not formed synchronously, their deposition on the carbon support (and stabilization against further growth as such) is a stochastic process, which results in a wide range of particle sizes. Some particles might also be deposited without being captured by the carbon support.

The XRD patterns of the catalysts are shown in Fig. 2. The broad reflection centred about $2\theta = 25°$ is the graphite (0 0 2) diffraction from the carbon support [8]. For both catalysts, strong diffraction peaks at Bragg angles of 39.8°, 46.3°, 67.5° and 81.3° are detected and can be indexed to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of face centred cubic (fcc) Pt.

Wide-scan XPS spectra of Pt-1/C and Pt-2/C reveal only the presence of C, O and Pt, without any trace of boron. The Pt 4f spectra of Pt-1/C and Pt-2/C are given in Fig. 3. In Fig. 3(a), the more intense doublet at 71.44 and 74.74 eV is a signature of metallic Pt, while the less intense doublet at 72.84 and 76.04 eV is often assigned to oxidized Pt in the divalent state such as PtO and Pt $(OH)_2$ [9]. The Pt 4f spectrum of Pt-2/C (Fig. 3(b)) can be deconvoluted into three doublets, with the doublet at 71.71 and 75.04 eV to Pt(0), the doublet at 72.71 and 76.04 eV assignable to Pt(2), and the doublet at 73.83 and 78.20 eV to Pt(4) [10,11]. One would have expected a higher Pt(0) content