Characterisation of carbon supported platinum-ruthenium fuel cell catalysts of different degree of alloying

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ABSTRACT

A series of PtRu/C fuel cell catalysts have been characterised by a combination of transmission electron microscopy, scanning transmission electron microscopy, energy dispersive X-ray microanalysis, X-ray diffraction and inelastic incoherent neutron scattering. The diffraction and microscopy studies show that a range of catalysts with different degrees of alloying can be obtained. It was possible to produce a strongly alloyed catalyst with average particle size below 10 nm. STEM/EDX results on the local compositions of the precious metal particles of different size and composition showed that the larger the particles the larger the Pt/Ru ratio. This indicates that ruthenium appears to prevent the agglomeration of the platinum particles to retain the smaller nanometer size. Inelastic neutron scattering spectroscopy shows that on the alloyed catalysts hydrogen occupies the threefold site, with no evidence for occupation of the on-top sites even under 800 mbar of hydrogen gas. Changes in the region of the out-of-plane C–H vibrational bands of the carbon black support indicated a contribution of the support during catalyst formation treatment by carbothermal reaction at lower temperature. Comparison of HREELS data from single crystal work and vibrational energy values from neutron spectroscopy allows to derive information on the site occupation of atomic hydrogen on finely divided precious metal particles supported on highly absorbing high surface area carbon blacks.

1. Introduction

For automotive applications, electric motors driven by fuel cells offer considerable advantages over gasoline or diesel engines. The major advantages are that fuel cells are non-polluting at the point of use and are at least twice as energy efficient as internal combustion engines [1]. The low temperature fuel cells e.g. proton exchange membrane fuel cell or direct methanol fuel cell that are used for transport applications require a catalyst on the anode to dissociate the dihydrogen fuel to protons and electrons. Carbon black supported platinum (Pt/C) catalysts are the electrocatalytic materials of choice for this application [2].

Unfortunately Pt/C catalysts are very susceptible to poisoning by carbon monoxide. This necessitates the use of very pure dihydrogen as a feed which increases costs. Recent work has been directed at producing carbon monoxide tolerant platinum catalysts by alloying with another metal. A variety of metals have been used but ruthenium is usually the preferred metal [3]. Atomic ratios ranging from 1:9 to 9:1 Pt:Ru have been investigated [4,5], but 1:1 Pt:Ru is generally used [3]. The catalysts have been prepared by a variety of routes [3,5–7], although most often by co-precipitation. There has been considerable work on characterising the catalysts by a variety of spectroscopic [5–9] and diffraction methods [10,11], particularly with the aim of investigating whether the platinum and ruthenium present are alloyed or phase separated.

In previous work on Pt/C fuel cell catalysts [12,13] we have used a combination of electron microscopy and incoherent inelastic neutron scattering (IINS) to characterise the metal particles and the adsorption sites of adsorbed hydrogen. IINS is a form of vibrational spectroscopy where the scattered intensity depends on the number of scattering centres, the amplitude of vibration and the inelastic scattering cross section [14]. The cross section is large for hydrogen and small for virtually all other elements. Thus both the carbon support and the metal are essentially transparent to neutrons. Further, since the scattering is by the nucleus, there are no selection rules so all modes are allowed and, in principle, observable. The use of IINS for catalyst research has recently been reviewed [15].

2. Experimental

2.1. Catalyst preparation

Four samples were prepared according to the preparation processes described in Refs. [16,17] and modified for the preparation of the bimetallic catalysts in EP0880188 to give a catalyst that was 60 wt% metal and with a nominal 1:1 Pt:Ru ratio. Briefly described the preparation of the catalysts includes a co-precipitation of a 25% wt. hexachloroplatinum acid solution and a 20% wt. ruthenium chloride solution with sodium hydroxide and a consequent reduction by formaldehyde. Each of the four catalysts was treated in a different fashion as shown in Table 1 so as to produce a range of particle size and degree of alloying. Alloying was induced by reductive high-temperature annealing in a tube furnace under different conditions using N_2/H_2 (95/5) forming gas. For all the catalysts the same grade of high purity carbon black (Ketjen black EC300) was used as support material with a nitrogen surface area of 800 $m^2\,g^{-1}$. Since the solubility of hydrogen in platinum is very small [18], the adsorbed hydrogen will be located predominantly at the surface of the platinum particles.

2.2. X-ray diffraction

XRD was performed using a Panalytical XPERT-Pro θ/θ-System with CuKα radiation. The size of the precious metal particles was calculated using the Scherrer formula [19]. Lattice parameters were determined by total pattern fitting.

2.3. Electron microscopy

A Jeol 2010F field emission transmission electron microscope (TEM) with a scanning unit (STEM) was operated at 200 keV acceleration voltage. For spot analysis of the precious metal particles by energy dispersive X-ray analysis (EDX) a Noran SiLi detector with a 30 mm^2 crystal and a Noran system six device was used.

A catalyst sample was dispersed in chloroform and transferred onto holey carbon foil supported by a 200 mesh copper grid. For statistical evaluation of the primary particle sizes of the supported precious metal entities the I-TEM software of soft imaging systems (SIS), Münster, was utilized.

2.4. Inelastic Incoherent Neutron scattering

For each catalyst, ~40 g of PtRu/C was loaded into a thin walled aluminium can with a Viton O-ring seal and a Nupro valve. The surface oxide was removed by successive hydrogenation/evacuation cycles as described previously [12,13]. Slow hydrogenation at low hydrogen doses were carried out to avoid excessive heating of a catalyst and artificial particle growth due to hydrogenation.

IINS spectra were recorded with the TOSCA [14,20,21] spectrometer at ISIS [22] (Chilton, UK). TOSCA offers a broad spectral range (24–4000 cm^{-1}) and high resolution (1.25% of the energy transfer). IINS measurements were made on the hydrogenated samples with gaseous (0.8 bar sorption equilibrium pressure) H_2 present and on the catalysts dehydrogenated by heating to 473 K under vacuum for 30 min. The evacuated catalysts were used for background subtraction. Experience has shown that it is essential to use the clean sample as the background, using a similar sample as a background saves beam time (and hence increases the number of samples that can be measured) but reduces the reliability. All the spectra shown here use the clean sample as a background. Measurement times were ~12 h.

3. Results

3.1. X-ray diffraction and electron microscopy

XRD provides information on the phase composition of the catalysts and the average degree of alloying between Pt and Ru as shown by the lattice contraction: face centred cubic (fcc) Pt = 0.39240 nm, hexagonal close packed (hcp) Ru = 0.27059 nm,

Table 1
PtRu/C catalyst treatment and characterisation by X-ray diffraction and STEM/EDX.

| | Catalyst sample treatment and *outcome* | Phase composition by XRD[a] | Lattice parameter from XRD/nm | Ru:Pt ratio by STEM/EDX/(at.%/at.%) | Particle size | | |
					Fine particles by TEM/nm	Coarse particles by TEM/nm	XRD/nm
1	Dried, reduced and annealed to generate alloying but also particle growth *Partly alloyed*	fcc PtRu + (Pt and hcp Ru)	0.3877	60/40 54/45 52/48 35/65 35/65 33/67 23/77	2–3.5	20–35[b]	4.7
2	Dried, reduced and annealed to generate alloying but also particle growth *Strongly alloyed*	fcc PtRu + (hcp Ru)	0.3868	54/45 52/48 50/50 48/52 44/56 44/56	2–4	20–38[c]	23.5
3	Dried and reduced, not annealed *Weakly alloyed*	fcc Pt, + amorphous RuOx	0.3923	92/8 57/43 56/44 44/56 18/82 9/91 4/96	2–3	4–8	4.0
4	Dried, reduced and carefully annealed to generate a high degree of alloying without pronounced particle growth *Strongly alloyed*	fcc PtRu + (hcp Ru)	0.3869	56/44 52/48 50/50 49/41 48/51 45/55	7–12	Only few	8.0

[a] XRD reference values: Pt fcc 0.39240 nm, Ru hcp 0.27059 [22].
[b] Small number.
[c] Large number.