

In situ EXAFS investigation of carbon-supported Pt clusters under potential control

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The transformation of carbon supported Pt clusters under potential control in 1M HClO₄ solution was investigated by in-situ X-ray absorption spectroscopy measurements. Both XANES and EXAFS data are used to show the structure evolution of the Pt clusters at various potentials. It showed that the white line area and the edge energy increase with the applied potential in the range 0.1~1.5V. The coordination number of oxygen and platinum on the Pt/C electrode increases and decreases, respectively, with the applied potential. It is found that the size of Pt cluster does not grow during the electrode fabrication. However, the crystallization of Pt cluster occurs during the potential cycling.

Keywords: X-ray absorption, transformation, Pt cluster, crystallization

1. Introduction

In recent years a number of in situ and ex situ structure sensitive techniques have been applied to characterize electrochemical systems at the atomic level. The conventional and sensitive uhv techniques which rely on the emission or scattering of electrons have been used ex situ by coupling the uhv chambers to the electrochemical cell using appropriate transfer systems. While these techniques can identify species and give information about both chemistry and structure, they are clearly subject to a number of restrictions: surfaces may restructure on transfer and measurements or adsorbates are restricted to strongly chemisorbed species. To overcome these ambiguities, it is far more desirable to examine electrodes in situ, that is, in an environment, which closely duplicates that of the real device.

This optimal strategy, however, elicits a new set of challenges, derived from the need of finding suitable probes with which to view inside the cell. The recent advent of high intensity tunable sources of x-rays, now available at synchrotron facilities worldwide, have opened new prospects for studying materials to an extent far beyond simple imaging or crystal structure determination. The penetration power and elemental specificity of x-rays is the key to the development of new experimental strategies, which are now beginning to unveil various aspects of operating electrodes. The full exploitation of these capacities will undoubtedly lead to a better understanding of electrocatalysts by allowing us to look inside while the device is at work.

Ex situ EXAFS measurements have recently been carried out to study metal-carbon interactions in carbon-supported platinum catalysts, and the developing use of EXAFS for the study of electrocatalysts have been reviewed. The oxidation/ reduction of platinum electrodes in different solutions has been shown to be a complex process by many fundamental electrochemical studies. Meanwhile, the reactivity of metal clusters has been reported in the literature. Therefore, an improved understanding of the structure evolution of carbon-supported Pt clusters is essential under

potential control. Herron et al.(1992) have applied the XAS to investigate the structure evolution of carbon-supported Pt (Pt/C electrodes) in 1M H₂SO₄ at various potentials. The platinum crystallite size they used was in the range of 10-60 Å. Changes in the near-edge spectra and in the extended X-ray absorption fine structure are reported and discussed in terms of the structural nature of the surface oxidation process.

The objectives of the current study are to investigate in situ the transformation of carbon-supported platinum clusters with crystallite size of 20 Å under controlled potential conditions using X-ray absorption spectroscopy in 1M HClO₄. It will provide an improved understanding of the electrochemical behaviors of carbon-supported platinum clusters.

2. Experimental

The electrodes were fabricated using carbon-supported platinum cluster material with a mean cluster diameter of 2 nm, which was given by the supplier. The carbon-supported platinum electrodes are circular discs, 1.9 cm in diameter and 0.75 mm thick. These are made using fuel cell electrode fabrication techniques (Borthen et al., 2000). Each electrode contains 64 mg of 10% Pt on carbon, 10 mg of carbon fibers and 9 mg of PTFE. The platinum loading is 2.2 mg/cm² and the platinum surface is about 140 m²/g. The electrochemical characteristics of the electrode in deaerated 1M HClO₄ at 25°C were examined by cyclic voltammetry in a conventional three-compartment glass cell. The working electrode was the circular disc of the carbon-supported platinum electrode. A saturated calomel electrode, connected via a salt bridge to a Luggin probe, was positioned 1 mm from the working electrode. However, all the potentials reported here are with respect to SHE (standard hydrogen electrode). The counter electrode is a high surface area platinum mesh.

The XAS measurements were performed in a propose-designed cell at the HasyLab beamline X1.1 and the SRRC beamline BL17C. The electrochemical cell for the in-situ XAS study of electrocatalysts in an electrolyte environment was carefully designed to avoid excessive attenuation of the x-ray beam. During the experiments the working electrode was stepped from OCP to -0.1V first and then stepped to several potentials between 0.1V and 1.5V in deaerated 1M HClO₄ at 25°C. The current versus time transient was recorded during each perturbation and the electrode was allowed to reach a steady state. The spectra were recorded in the vicinity of the Pt L₃ edge when the electrode reaches the steady state at each potential. The intensity of the incoming X-ray beam as well as the transmitted intensity was measured using gas-filled ionization chambers. A third ionization chamber was used for a simultaneous recording of Pt foil spectra. The X-ray beam from the electron storage ring was monochromatized by a double-crystal monochromator with Si(111).

3. Results and Discussion

Figure 1 shows a typical cyclic voltammogram (CV) obtained for the carbon-supported Platinum cluster (Pt/C) electrode in 1M HClO₄ at 25°C between the potential of 0 and 1.2V vs. SHE. At potentials more positive than 0.7V, oxide formation occurs, while a broad oxide reduction peak is evident on the reverse sweep at a potential of ca. 0.6 V. Hydrogen adsorption is observed at potentials in the range 0.2 to 0 V on the negative sweep followed by hydrogen desorption in the range 0 to 0.2 as the potential is swept in the positive direction. On the basis of the CV behavior, potentials at 1.0, 1.2, and 1.5V, which correspond to increasing degrees of platinum oxidation, were chosen for in situ XAS measurements. Although the oxygen evolution occurs at 1.5V, the obtained XAS data is still good enough for analysis. After the XAS measurement at 1.5V, the electrode was stepped to 1.55V for 1 hr and then swept

to the other potential in the negative direction for the other XAS measurements.

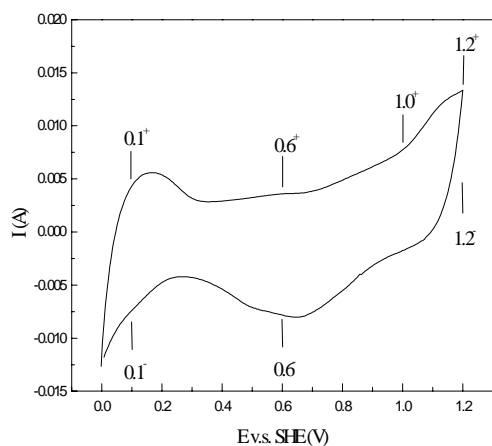


Figure 1

Cyclic voltammograms of carbon-supported Pt clusters electrode in 1M HClO₄ at 25°C (sweep rate 2mV/sec). (+ and - means positive and negative scans, respectively)

In Figure 2 the Pt L₃ near-edge absorption spectra recorded for the Pt/C electrode at various potential are compared with the spectra of Pt foil and α-PtO₂. Meanwhile, the white line area of different samples integrated in the near-edge range from -10 to 40 eV was shown in Table 1. This white line is due to electron transitions from the 2p to the d state and its height is related to the d-band character of the absorbing atoms.

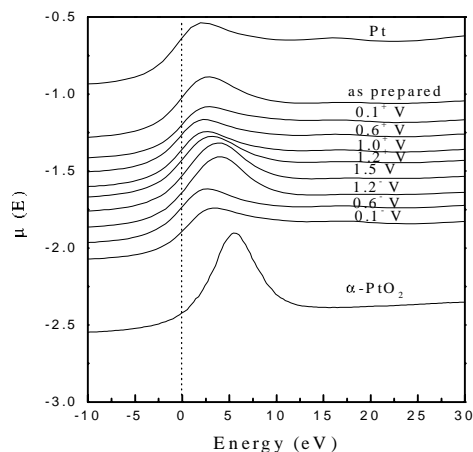


Figure 2

Pt L₃ near-edge absorption spectra of Pt foil, α-PtO₂, as prepared Pt/C electrode, and the Pt/C electrode at various potentials.

In Figure 3 the experimental k³-weighted EXAFS spectra recorded for the Pt/C electrodes are compared with the spectra of the model compounds. It was found that the spectra for the Pt/C electrode in the oxide region, i.e. 1.2 or 1.5 V, are visibly different from those in the metal region, i.e. 0.1 or 0.6 V. Figure 4 shows the Fourier transforms of these spectra. These transform have not been corrected for the phase shifts of the central or backscattering atoms. It shows more clearly that the changes in the modulus of Fourier

transform occurs as the potential varies. For Pt foil, the main peak in the Fourier transform is due to the back scattering from twelve nearest-neighbour atoms of Pt. The shoulder in front of the main peak arises from a structure in the backscattering amplitude of Pt atoms. The main peak of the Pt/C electrode is smaller than that of the Pt foil. It reflects the small size of Pt clusters in the Pt/C electrode. In the oxide formation region, the amplitude of this peak decreases and a new peak corresponding to the nearest-neighbour oxygen appears at a lower distance from the central atom. The two-shell fits (dashed line) with the backtransformed experimental data (solid line) at various potentials were rather good (data not shown here). The obtained parameters involving the shell distances, coordination numbers, Debye-Waller factor, and the threshold energy were shown in Table 1.

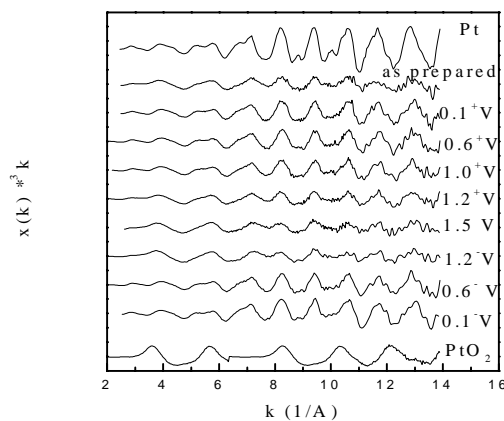
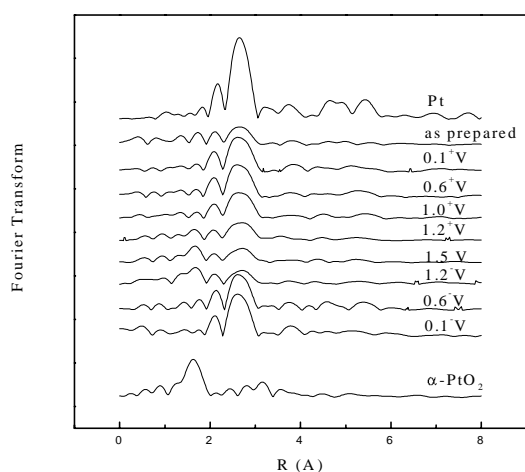


Figure 3

k³-weighted experimental Pt L₃ EXAFS spectra of Pt foil, α-PtO₂, as prepared Pt/C electrode, and the Pt/C electrode at various potentials.

Both XANES and EXAFS data can provide information on the oxidation state of Pt atom of the clusters on carbon. From the data of edge shift, white line area and the coordination number of oxygen, it indicates that as-prepared Pt/C electrode is on the oxidation state. The edge energy shifts to lower energy and the white line area becomes smaller compared to those of as-prepared Pt/C electrode when the applied potential is 0.1V. Although the edge shifts are insignificant as the potential is stepped to 0.6⁺ and 1.0⁺V, the data of the increasing of the white line area as well as coordination number of oxygen and decreasing in the coordination number of platinum shows that the Pt clusters are slightly oxidized or strongly hydrated in the potential range 0.6⁺~1.0⁺V. As the potential increases to the oxide formation region (larger than 1.0⁺V), the white line area increases obviously. Meanwhile, the coordination of the oxygen increases, while the coordination number of platinum decreases as the applied potential increases. However, the white line area at highest potential is still smaller than that of the α-PtO₂. It suggests that the oxidized Pt clusters might consist of a mixture of metallic Pt (in the cluster core) and oxidized Pt (at the cluster surface). It is interesting to know whether the Pt clusters can be completely oxidized. The Pt/C electrode was kept at the potential of 1.55V and with continuously taking XAS measurements. Unfortunately, the S/N ratio is bad due to severe oxygen evolution at this potential. After that, the potential was stepped to 1.2V and the XAS measurements were performed. The coordination numbers of oxygen and platinum further increases and decreases, respectively. The white line area is also increased. This result indicates that the Pt/C electrode can be further


Figure 4

Fourier transforms of the EXAFS spectra of Pt foil, α -PtO₂, as prepared Pt/C electrode, and the Pt/C electrode at various potentials.

Table 1

The structure parameters obtained from the best fits of the EXAFS spectra for the carbon-supported Pt cluster electrodes in 1M HClO₄ at various potential.

Samples	E/V(SHE)	Atom	N	R/Å	$\sigma^2/\text{Å}^2$	$\Delta E_0/\text{eV}$	W_A
Pt foil	-	Pt	12	2.77	0.0027	-1.8	4.95
Pt/C	As-prepared	O	1.2	2.08	0.0027	-1.7	4.78
		Pt	6.1	2.77	0.0051	-4.2	
Pt/C	0.1 ⁺	Pt	9.5	2.76	0.0041	-2.4	4.15
Pt/C	0.6 ⁺	O	1.3	2.13	0.0096	-1.0	4.40
		Pt	8.7	2.76	0.0040	-1.9	
Pt/C	1.0 ⁺	O	1.4	2.09	0.0096	-1.0	4.44
		Pt	8.1	2.76	0.0045	-2.3	
Pt/C	1.2 ⁺	O	2.4	2.07	0.0063	-1.8	5.46
		Pt	5.2	2.77	0.0040	-3.4	
Pt/C	1.5	O	3.7	2.05	0.0060	-0.1	5.65
		Pt	3.8	2.77	0.0042	-4.4	
Pt/C	1.2 ⁻	O	4.2	2.04	0.0061	0.5	5.97
		Pt	3.6	2.78	0.0041	-6.3	
Pt/C	0.6 ⁻	O	1.0	2.14	0.0025	-5.1	4.27
		Pt	7.6	2.77	0.0035	-4.3	
Pt/C	0.1 ⁻	Pt	10.5	2.76	0.0044	-0.5	4.01
α -PtO ₂	-	O	6	2.05	0.070	-28	7.45
		Pt	6	3.09	0.069	-28	

OCP is the open circuit potential, N is the coordination number, r is the neighbour shell distance, σ^2 is the structural disorder term, WA is the white line area.

+ and - means positive and negative scans, respectively.

oxidized even the potential was 1.2V at the negative scan. However, it seems difficult to oxidize the clusters completely. When the potential was stepped to 0.6V, the white line area and the coordination number of the Pt-O shell decrease but the coordination number of the Pt-Pt shell increases. Note that the S/N ratio of the EXAFS spectra at the same potential is better for the negative scan compared to the positive scan. Meanwhile, the coordination number of the platinum clusters becomes 10.5, which is larger than 9.5 obtained at first reduction potential of 0.1⁺V. From the coordination number of the platinum, the cluster size can be estimated. After the first reduction of the Pt clusters, their size is about 20 Å estimated from the Pt coordination number of 9.5. It is consistent with data reported by the supplier. This result also indicates that the cluster size does not grow during the fabrication of the electrode. However, the cluster size becomes ca. 35 Å estimated from the Pt coordination number of 10.5 after this potential cycling. Therefore it can be concluded that the Pt clusters have recrystallized and enlarged during the potential sweep.

Comparison of the bond distance of Pt-O of the Pt/C electrode at higher and lower potential, it was shown that the bond distance becomes shorter as the potential is higher. It might suggest the formation of hydrated oxide (Pt-OH) at lower potential but oxide (PtO₂) at higher potential. In addition, it was found that the threshold energy is a more negative value, as the potential is higher. It is interesting but needs to be further investigated.

4. Conclusion

The transformation of carbon-supported platinum clusters under potential control was investigated using in-situ XAS measurements in 1M HClO₄ in this study. It provided a more deep insight into the state and structure evolution of carbon-supported platinum clusters. It was found that the oxidized Pt clusters might consist of a mixture of metallic Pt (in the cluster core) and oxidized Pt (at the cluster surface). Although, the size of Pt clusters does not grow during the electrode fabrication of commercial Pt/C materials, the crystallization of Pt clusters occurs during the potential cycling. This presumably yields an activity decay of the Pt/C electrode as observed during its applications in fuel cells and sensors.

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