

# CO surface diffusion on platinum fuel cell catalysts by electrochemical NMR<sup>☆</sup>

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## Abstract

We report on surface CO diffusion processes in relation to properties of nanoparticle Pt and Pt/Ru fuel cell catalysts. The CO<sub>ad</sub> diffusion was studied by the use of <sup>13</sup>C electrochemical nuclear magnetic resonance (EC-NMR) spectroscopy. Measurements were carried out in the temperature range 253–293 K, where the solution side of the nanoparticle–electrolyte interface is liquid, in contrast to previous measurements, in ice. We offer a concerted view of the effect of particle size and surface coverage on CO<sub>ad</sub> diffusion, and find that both are important. We also found that the diffusion parameters were influenced by the variations in the distribution of chemisorption energies on particles of different sizes, and by the CO–CO lateral interactions. On all Pt nanoparticle surfaces investigated, we conclude that CO surface diffusion is too fast to be considered as the rate-limiting factor in methanol reactivity. The addition of Ru to Pt increases the surface diffusion rates of CO, and there is a direct correlation between the Fermi level local density of states ( $E_F$ -LDOS) of the 2 $\pi^*$  molecular orbital of adsorbed CO and the activation energy for surface diffusion. These results are of interest since they improve our knowledge of surface dynamics of molecules at electrochemical interfaces, and may help to formulate better models for the electrooxidation of adsorbed CO on nanoparticle surfaces.

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**Keywords:** Surface diffusion; NMR; Adsorbed CO; Pt nanoparticles; Pt/Ru nanoparticles; CO coverage; Particle size effect

## 1. Introduction

Molecular surface motions are one of the prime topics of electrochemical surface science [1–9]. In particular, CO surface diffusion on catalytic electrode surfaces needs to be understood as it may help to identify the rate limited reactions of relevance to fuel cell reactivity [7–9]. CO<sub>ad</sub> diffusion on Pt surfaces has been extensively investigated under ultra-high vacuum or gas phase conditions [2,3,9–12]. However, prior to our reports [8], surface diffusion of CO on platinum electrodes in liquid electrochemical environment had not been measured directly at and near room temperature, although some estimates had been made based on indirect methods [6,13,14], or in ice [15,16]. (Notice the STM study of sulfur/sulfide motions on copper single crystal electrodes in chloride media [17], of a clear relevance to

this study.) Electrochemical nuclear magnetic resonance (EC-NMR) spectroscopy is one of the rare techniques that permits a detailed study of the electronic structure of electrodes and adsorbates [7,15,18–27]. It has a distinct advantage over many other surface science techniques that both nanoparticle catalysts and adsorbates can be investigated and the NMR parameters (spectra and relaxation rates) can be interpreted in terms of the Fermi level local density of states ( $E_F$ -LDOS). Moreover, the capability of EC-NMR method in studying surface diffusion at the solid–liquid interface at and near room temperature has already been demonstrated [8,9], and is further developed in this lecture.

In this work, we review some of our CO surface diffusion data obtained on a Pt-black electrode in the broad range of CO coverage [9]. We also present some new data obtained with C-supported small Pt and Pt/Ru nanoparticles of commercial fuel cell catalysts [9]. We notice that the roles of CO<sub>ad</sub> coverage-dependent lateral interactions [28], as well as those of the CO adlayer structure [29,30] in determining the rates of CO surface diffusion are not yet understood. We have therefore carried out a detailed study of the effects of CO surface coverage on the activation barriers for CO diffusion, as well as on the pre-

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exponential factors [9], and demonstrate a sizable particle size effect on CO diffusion coefficients. Namely, we will show below that the value of the CO diffusion coefficient is reduced by up to an order of magnitude between ca. 7 and 3 nm catalyst samples.

## 2. Experimental

### 2.1. Sample preparation and CO<sub>ad</sub> dosing procedure

About 300 mg of fuel cell grade polycrystalline platinum black (Pt-black, Johnson-Matthey, MA) was electrochemically cleaned in 0.5 M H<sub>2</sub>SO<sub>4</sub> in D<sub>2</sub>O (99% enriched, Sigma–Aldrich) by voltammetric cycling [8,9] and by holding the electrode potential at 0.46 V (vs. RHE) for 15 min [31]. New data were obtained with carbon-supported Pt (2.6 nm) nanoparticle catalysts received (as a gift) from Tanaka Comp. After the cleaning procedure was completed, CO adlayers were produced either by bubbling <sup>13</sup>C (99%)-enriched CO (Cambridge Isotopes, MA) through the electrolyte, or by catalytic decomposition of <sup>13</sup>C-enriched methanol. As already documented, the type of chemisorbed CO on platinum does not depend on the source of CO [19]. To prepare the sample with  $\theta = 1.0$  (saturation coverage of CO<sub>ad</sub>) and of  $\theta = 0.68$ , <sup>13</sup>CO was adsorbed by admitting the <sup>13</sup>CO gas to the electrolyte at an open-circuit potential (ca. 0.2 V after CO adsorption), followed by purging the electrolyte with ultra-pure argon, to remove excess CO [8]. To prepare CO<sub>ad</sub>–Pt samples at  $\theta \leq 0.5$ , the <sup>13</sup>C (99%)-enriched methanol (Cambridge Isotopes, MA) was directly decomposed on the Pt

catalysts [22]. For instance, the sample with  $\theta = 0.46$  was prepared by holding the potential at 0.4 V for 4 h in a solution of 100 mM methanol in 0.5 M H<sub>2</sub>SO<sub>4</sub>. For preparing the sample with  $\theta = 0.36$ , Pt catalysts were held at 0.4 V for 16 h in a solution of 2 mM methanol in 0.5 M H<sub>2</sub>SO<sub>4</sub>. For preparing CO adsorbed on Pt/C sample with  $\theta = 0.54$ , Pt/C catalysts were held at 0.4 V for 20 h in a solution of 35 mM methanol in 0.5 M H<sub>2</sub>SO<sub>4</sub>. At the end of the CO adsorption cycles (from methanol), excess electrolyte was removed and the cell was refilled with pure 0.5 M D<sub>2</sub>SO<sub>4</sub>. The rinsing procedure was repeated six times. The NMR samples were transferred to glass ampoules along with the electrolyte and then flame sealed [21]. A small amount of sample was left in the electrochemical cell, to permit the determination of the CO coverage, estimated from the oxidation charge in stripping voltammetry (assuming that the oxidation of a CO monolayer requires 420  $\mu\text{C cm}^{-2}$  of Pt with respect to hydrogen adsorption charge, 210  $\mu\text{C cm}^{-2}$  of Pt). Since CO desorption from Pt surfaces and CO<sub>ad</sub> migration between C-supported nanoparticles is known to be negligible, we do not expect any significant variations in CO coverage between different particles. This is also a pre-requisite for particle size effects, which we report below.

### 2.2. NMR experiments

We use the “S-shape” pulse sequence [33] (Fig. 1a) for the measurement of CO surface diffusion. As described elsewhere [8,33], this sequence consists of a spin echo sequence preceded by a selective inversion sequence. Part of the spins are inverted

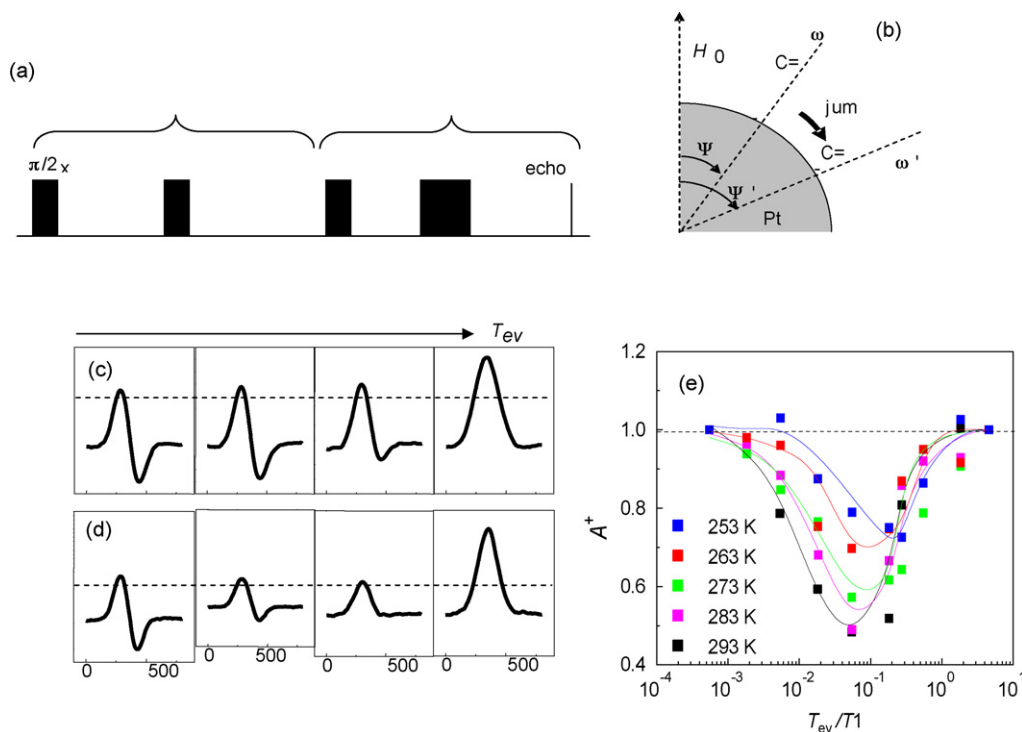


Fig. 1. (a) The S-shape pulse sequence, based on Ref. [33]. (b) Schematic diagram of CO surface diffusion altering the <sup>13</sup>C Larmor frequency ( $\omega$ ). NMR line shapes obtained for the S-shape pulse sequence and their evolution with  $T_{ev}$ . (c) At 120 K (no diffusion), the amplitude of the positive part,  $M^+(T_{ev})$ , grows back monotonically to its thermal equilibrium. (d) At 293 K (fast diffusion), the amplitude  $M^+(T_{ev})$  initially decreases due to the mixing of non-inverted and inverted spin magnetization, as a result of surface diffusion. (e) Variation of  $A^+$  in the S-shape experiment for the  $\theta = 0.46$  sample. At  $T = 120$  K,  $A^+ = 1$  for all  $T_{ev}$  values, showing no mixing of inverted and non-inverted spins. At  $T = 293$  K,  $A^+ < 1$ , due to spin mixing [9].

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