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

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#### ostract

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 died by the use of <sup>13</sup>C electrochemical nuclear magnetic resonance (EC-NMR) spectroscopy. Measurements were carried out in the temperature nge 253–293 K, where the solution side of the nanoparticle–electrolyte interface is liquid, in contrast to previous measurements, in ice. We offer concerted view of the effect of particle size and surface coverage on  $CO_{ad}$  diffusion, and find that both are important. We also found that the fusion parameters were influenced by the variations in the distribution of chemisorption energies on particles of different sizes, and by the D–CO lateral interactions. On all Pt nanoparticle surfaces investigated, we conclude that CO surface diffusion is too fast to be considered as the e-limiting factor in methanol reactivity. The addition of Ru to Pt increases the surface diffusion rates of CO, and there is a direct correlation tween 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 fusion. These results are of interest since they improve our knowledge of surface dynamics of molecules at electrochemical interfaces, and may lp to formulate better models for the electrooxidation of adsorbed CO on nanoparticle surfaces.

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

#### Introduction

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

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13-4686/\$ – see front matter © 2008 Elsevier Ltd. All rights reserved. :10.1016/j.electacta.2008.02.046 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  $CO_{ad}$  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-

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 MH<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  $CO_{ad}$ ) 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  $CO_{ad}$ -Pt samples at  $\theta \le 0.5$ , the <sup>13</sup>C (99%)-enriched methanol (Cambridge Isotopes, MA) was directly decomposed on the Pt

(a)

 $\pi/2_{\rm X}$ 

(c)

(d)

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  $\mu$ C cm<sup>-2</sup> of Pt with respect to hydrogen adsorption charge,  $210 \,\mu\text{C}\,\text{cm}^{-2}$  of Pt). Since CO desorption from Pt surfaces and COad 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

(b)

ium



echo

1.2

1.0

8.0 4 (e)

253 K

Tev

the first two 90° pulses and are then allowed to diffuse on e surface during the evolution period,  $T_{ev}$ . The surface difsion of a CO<sub>ad</sub> molecule can alter the relative orientation tween the <sup>13</sup>CO<sub>ad</sub> molecular axis and the external magnetic ld (Fig. 1b) which changes the <sup>13</sup>C spin's Larmor frequency. is will lead to a change in the net nuclear magnetization, nich can be monitored through intensity changes in the NMR ectrum. When adsorbed CO molecules do not undergo any surce diffusion, the non-inverted part of the magnetization, and nce the normalized signal amplitude  $(M^+(T_{ev}))$ , grows back onotonically to its thermal equilibrium value with increasg  $T_{\rm ev}$ , as shown in Fig. 1c. However, if CO<sub>ad</sub> molecules dergo surface diffusion during  $T_{ev}$ , then the mixing of the verted and non-inverted spin magnetization leads to an initial crease in the amplitude  $M^+(T_{ev})$  of the non-inverted part of e spectrum (Fig. 1d) before it grows back to its thermal equirium value.  $M^+(T_{ev})$  is measured experimentally for various lues of  $T_{ev}$  and then compared with a theoretically calculated  $^{+}(T_{ev})$  value, assuming no diffusion contributions. In order calculate the diffusion coefficient ( $D_{CO}$ , in cm<sup>2</sup> s<sup>-1</sup> units 4]), we follow a normalized signal amplitude,  $A^+$ , defined a ratio of  $(M^+(T_{ev})$  with diffusion)/ $(M^+(T_{ev})$  without diffuon), as a function of  $T_{ev}$ . The contribution due to the mixing of verted and non-inverted spins resulting from surface diffusion CO can be seen as a trough in the  $A^+$  values when plotted ainst  $T_{\rm ev}/T_1$  (Fig. 1e). More details of the extraction of the ffusion constant/activation barriers can be found elsewhere

<sup>13</sup>C NMR measurements were carried out at 8.47 T using a ome-built" NMR spectrometer [35]. Typical 90° pulse widths 8-12 µs and a 30-µs delay were used for echo detection. The -value (Fig. 1a) used in all cases was  $8 \mu s$ , while  $T_{ev}$  was ried from 80  $\mu$ s to 1.5 s. <sup>13</sup>C  $T_1$  values were obtained by using inversion-recovery technique. Experiments were carried out tween 253 and 293 K at 10 K intervals using a continuous flow yostat (CF-1200, Oxford Instruments, MA) on four samples CO adsorbed on Pt-black, having coverages of  $\theta = 1.0, 0.68$ , 46 and 0.36. The <sup>13</sup>C NMR signal showed a broad, single aussian peak and there was no indication of any CO present in e electrolyte, which would have resulted in a sharp resonance at 181 ppm. The chemical shifts for <sup>13</sup>C are reported with respect tetramethylsilane (TMS) using the IUPAC  $\delta$ -scale in which gh frequency, low-field, paramagnetic or deshielded values are sitive.

## **Results and discussion**

## 1. Methanol oxidation, DMFC fuel cell relevance

It is well known that on Pt sites of the Pt/Ru catalyst of DMFC irrect oxidation methanol fuel cell) methanol decomposes to rface CO, and the CO<sub>ad</sub> formed on Pt is transported via surface ffusion to a Pt/Ru boundary to be oxidized to CO<sub>2</sub> [36–38]. Ince the Pt/Ru site is relieved of CO<sub>ad</sub> via transformation to  $D_2$ , the catalyst surface has a lower CO coverage, and the catylic cycle of methanol transformation to CO<sub>2</sub> on a CO-free Pt sembly [39] continues according to the turnover rate principle

in heterogeneous catalysis [40], under steady-state conditions [39].

We now focus on  $CO_{ad}$  transport from Pt sites of the Pt/Ru catalyst to the Pt/Ru boundary. In the methanol decomposition process, two cases of the Pt/Ru catalyst composition can be envisaged: the first is the low Ru coverage, where  $CO_{ad}$  needs to hop over several inter-atomic Pt–Pt distances to the Pt/Ru boundary, and the second is the high Ru coverage, where  $CO_{ad}$  is present on the Pt site very near the Pt/Ru edge. At high Ru coverage, there is no room for  $CO_{ad}$  motions to affect methanol fuel cell reactivity, and this report concerns the case – and discusses respective fuel cell reactivity issues – where the  $CO_{ad}$  path to the Pt/Ru edges is long.

#### 3.2. NMR measurement of diffusion parameters

Becerra et al. [33] were the first to use the "S-shape" pulse sequence employed in this study, to measure diffusion of CO adsorbed on alumina-supported Pt nanoparticles under gas phase conditions. They reported diffusion parameters for samples with three different Pt dispersions and two different CO surface coverages. The activation energies for surface diffusion ( $E_d$ ) were found to lie in the range 6.5–10.5, kcal mol<sup>-1</sup> and a typical value of the pre-exponential factor,  $D_{CO}^0$ , was ~6 × 10<sup>-7</sup> cm<sup>2</sup> s<sup>-1</sup>. The activation energy increased from 7.4 to 10.5 kcal mol<sup>-1</sup> when the Pt dispersion (fraction of surface Pt atoms) was increased from 23% to 73%. Though both  $E_d$  and  $D_{CO}^0$  changed with CO coverage, no systematic variations could be inferred from this gas phase study [33].

In contrast to these results, we find here a strong systematic dependence of  $E_a$  and  $D_{CO}$  on CO surface coverage [7–9]. When the  $D_{CO}$  results are plotted as a function of  $T^{-1}$  for the four different CO<sub>ad</sub> coverages (Fig. 2), we find in each case typical Arrhenius behavior,  $D_{CO} = D_{CO}^0 \exp(-E_d/RT)$ . Moreover, it



Fig. 2. Variation of the diffusion coefficients with temperature for different CO coverages,  $\theta$ , on Pt-black (see Fig. 4). Straight lines correspond to the Arrhenius fits which yield the activation energies and pre-exponential factors given in Table 1 [9].

#### Table 1

Surface diffusion parameters ( $E_d$  and  $D_{CO}^0$ ) for CO<sub>ad</sub> on platinum, and the CO diffusion coefficient ( $D_{CO}$ ) at the temperature of 293 K as a function of converge in various environments [9]

Sample	$\theta$ (CO coverage)	$E_{\rm d}  (\rm k cal  mol^{-1})$	$D_{\rm CO}^0  ({\rm cm}^2  {\rm s}^{-1})$	$D_{\rm CO}~({\rm cm}^2{\rm s}^{-1})$	Ref.
In electrolyte					
Pt-black (ca. 7 nm)	1.00 <sup>a</sup>	$6.0 \pm 0.4$	$(1.1 \pm 0.7) \times 10^{-8}$	$3.6 \times 10^{-13}$	[8,9]
	0.68 <sup>a</sup>	$6.7 \pm 0.6$	$(4.8 \pm 2.3) \times 10^{-8}$	$8.1 \times 10^{-13}$	[9]
	$0.46^{a}$	$8.0\pm0.8$	$(8.8 \pm 4.0) \times 10^{-7}$	$9.5 \times 10^{-13}$	[9]
	0.36 <sup>a</sup>	$8.4\pm0.8$	$(3.7 \pm 1.9) \times 10^{-6}$	$1.5 \times 10^{-12}$	[9]
Pt-black (ca. 8 nm)	$\sim 0.5^{a}$	$7.9 \pm 2.0$			[15]
$Pt/GC (3.1 \text{ nm})^{b}$	$0.65 - 0.75^{\circ}$			$3-4 \times 10^{-14}$	[5]
$Pt/GC (1.7 \text{ nm})^{b}$	0.8–0.93 <sup>c</sup>			$7 \times 10^{-17}$	[5]
In gas phase/UHV					
$Pt/Al_2O_3$ (10 nm)	0.5	$6.5 \pm 0.5$	$6 \times 10^{-7}$		[33]
Pt(111)	0.1	$4.7 \pm 0.1$	$(1.4 \pm 0.4) \times 10^{-6}$		[12]
Pt(111)	0.67	$3.0 \pm 0.1$	$(4.5 \pm 1.0) \times 10^{-7}$		[12]

<sup>a</sup>  $\theta_{CO}$  was estimated from CO oxidation charge obtained from cyclic voltammetry, with respect to hydrogen adsorption.

<sup>b</sup> Electrochemical measurements.

<sup>c</sup>  $\theta_{CO}$  was deduced from CO oxidation at a constant potential.

can also be seen from Fig. 2 that  $D_{CO}^0$ ,  $E_d$  and  $D_{CO}$  are all coverage dependent: the activation energy increases from 6.0 to 8.4 kcal mol<sup>-1</sup> while the pre-exponential factor increases from  $1.1 \times 10^{-8}$  to  $3.7 \times 10^{-6}$ , when the CO<sub>ad</sub> coverage is reduced from  $\theta = 1.0$  to 0.36. For purposes of comparison, the Arrhenius parameters previously obtained for CO adsorbed and measured in the gas phase on supported Pt catalysts [33] and on a single crystal in UHV<sup>7</sup> are shown in Table 1.

For  $\theta = 1.0$ , we used Pt-black saturated with adsorbed CO ( $\sim 100\%$  CO coverage), so the surfaces of our sample have essentially no vacant Pt sites. However, a nanoparticle surface still provides a variety of sites with different coordination number "Z" of adsorption sites [41-43] where CO can adsorb with different binding energies. The differences between adsorption energies of CO bound to various sites lead to a chemical potential gradient between different CO<sub>ad</sub> populations. We therefore propose that the surface diffusion observed here is due to CO<sub>ad</sub> exchange between different surface sites, a mechanism similar to that seen for diffusion of long-chain alkanes at solid/gas interfaces [44]. More specifically, Han and Ceder [43] indicated that vertex, edge (111) and (100) surface sites are present on a nanoparticle sample (having the size from 1 to 2 nm [43]) with different coordination number "Z" of the adsorption sites. All sites display different adsorption energies for O and OH which are sensitive to the coordination number and the size of the Pt particles. The overall trend is that the adsorption energy increases as the Pt atom(s) involved in the adsorption become less coordinated by other Pt. We believe that the same effect will occur with CO chemisorption (of the fully CO covered Pt surfaces) in terms of the distribution of the CO<sub>ad</sub> binding energies between the vertex, edge  $(1 \ 1 \ 1)$  and  $(1 \ 0 \ 0)$  surface sites of the nanoparticle surface.

As mentioned above, we found a clear CO coverage effect on CO surface diffusion [9]. Namely, when the CO coverage is reduced from  $\theta = 1$  to 0.68,  $E_d$  increases from 6.0 to 6.7 kcal mol<sup>-1</sup> [9]. With further decreases in CO coverage ( $\theta = 0.46$  and 0.36), the activation energy increases to ~8.0 kcal mol<sup>-1</sup>. The  $E_d$  values (6–6.7 kcal mol<sup>-1</sup>) for the high coverage samples ( $\theta = 1.0$  and 0.68) compare well with 6.5 kcal mol<sup>-1</sup>, the  $E_d$  value reported for CO<sub>ad</sub> diffusion on alumina-supported Pt in gas phase at  $\theta = 0.5$  [33]. In this gas phase experiment as well as in some earlier ultra-high vacuum (UHV) investigations, the activation energy for CO surface diffusion ( $E_d$ ) was also reported to be coverage dependent [12,33,46].

To interpret the data we use an operational equation that assumes that  $E_d$  for CO surface diffusion varies linearly with CO<sub>ad</sub> coverage ( $E_d = E_d^0 + r\theta$ , where  $E_d^0$  is the activation energy for CO surface diffusion at zero coverage). This equation echoes the Frumkin term:  $\Delta G_{\theta}^0 = \Delta G_{\theta=0}^0 + r\theta$ , where  $\Delta G_{\theta}^0$  is the apparent standard-free energy of adsorption,  $\Delta G_{\theta=0}^0$  is  $\Delta G_{\theta}^0$ at zero coverage and *r* is the Frumkin interaction parameter [47,48].

In Fig. 3, we show the coverage dependence of the CO surface diffusion parameters,  $E_d$  and  $D_{CO}^0$ . For partial coverages,  $E_{\rm d}$  decreases linearly (Fig. 3a) and  $D_{\rm CO}^0$  decreases exponentially (Fig. 3b) with coverage. From the straight line fit (Fig. 3a), we can obtain the  $E_d^0$  value, and the slope of the fit gives the interaction parameter, r [47,48]. We obtain the  $E_d^0$  value of  $10.4 \pm 1.6 \text{ kcal mol}^{-1}$ , about twice as large as the  $E_d^{0}$  value obtained for CO<sub>ad</sub> diffusion on Pt(111) under UHV conditions [12]. This observation implies that the morphological features discussed above, as well as the presence of the electrochemical double layer [8], may hinder surface diffusion of adsorbed CO in an electrochemical environment. The interaction parameter  $(r = -5.4 \pm 2.9 \text{ kcal mol}^{-1})$  is comparable to that reported for CO on Pt(111) in UHV  $(-2.9 \pm 0.4)$  (12). Assuming that the analogy between our equation and the Frumkin term is correct, the large negative value for r indicates that repulsive CO–CO interactions dominate the coverage dependence of  $E_d$  (Fig. 4).

Although the  $E_d$  vs. CO coverage relationship we observe is similar to that seen with single crystal planes in UHV [12,49],

e actual magnitude of  $E_{d}$  for the nanoparticle surfaces is likely depend on the binding energy variations amongst differt adsorption sites [12], as discussed previously [43,50] (and so, indirectly, Refs. [41–43]). The EC-NMR value of  $D_{CO}^0$  of  $8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  for  $\theta = 0.46$  is quite close to that for surface ffusion of CO on 10 nm Pt nanoparticles supported on Al<sub>2</sub>O<sub>3</sub>  $\theta = 0.5$  (Table 1). The  $D_{CO}^0$  value for  $\theta = 1.0$  is the smallest in e series (Table 1), and as discussed before [8] the CO surface ffusion observed on Pt nanoparticle surfaces saturated with CO due to CO<sub>ad</sub> exchange, driven by the chemical potential gradit between different surface sites [6,44]. However, in the case nanoparticle Pt partially covered with CO, the free site hopng can clearly be a more effective mechanism, in which case, e pre-exponential factor becomes a function of CO coverage 1]. The free site hopping mechanism assumes that a diffusing sorbate stops when a collision takes place with another adsorte. This collision is assumed to be inelastic and it dissipates e kinetic energy of the diffusing adsorbate. The surface difsion coefficient is coverage dependent because the collision equency is higher, and the adsorbate mean-free path is lower, higher coverages. The pre-exponential factor will depend on e probability that a given CO<sub>ad</sub> molecule can find free sites its neighborhood. As shown in Fig. 3b,  $D_{CO}^0$  shows an expontial decrease with increasing CO coverage for the partially vered samples, and similar behavior has been observed for



g. 3. Coverage dependence of  $CO_{ad}$  diffusion parameters. (a) Variation of a activation energy with CO coverage. The straight line corresponds to the makin-type behavior (see text) for partially covered samples. (b) Variation the pre-exponential factor with CO coverage. The exponential fit (solid line) gests that for the partially covered samples ( $\theta < 1$ ), free-site hopping is the ncipal surface diffusion mechanism. The experimental points corresponding full coverage ( $\theta = 1$ ) are shown in red and indicate that the diffusion mecham for CO at  $\theta = 1$  is distinctively different from the free-site hopping model, plicable at partial coverage [9]. (For interpretation of the references to color this figure legend, the reader is referred to the web version of the article.)





Fig. 4. (a) TEM image and (b) histogram of platinum black (unsupported Pt nanoparticles, see text and Table 1). The average particle size of the majority group, 7 nm; the average nanoparticle size in the bimodal histogram, 10 nm (courtesy of N. Benker and C. Roth, TU Darmstadt).

the coverage dependence of surface diffusion of CO on Ru [52], where diffusion was attributed to free site hopping [51].

The results shown in Table 1 clearly indicate that CO coverage is a significant factor in CO surface diffusion events. It can also be seen (Fig. 3) that  $E_d$  as well as  $D_{CO}^0$  at  $\theta = 1.0$  do not fall on the solid lines, consistent with our previous suggestion [9] that the surface diffusion mechanism for fully CO covered sample is significantly different.

## 3.3. CO surface motions vs. fuel cell reactions in DMFC

In Fig. 2, we find typical Arrhenius behavior,  $D_{\rm CO} = D_{\rm CO}^0 \exp(-E_{\rm d}/RT)$  for each coverage for Pt-black. Also, the activation energies decrease linearly and the pre-exponential factors decrease exponentially with coverage (Fig. 3). In contrast, when C-supported 2.6 nm<sup>1</sup> platinum nanoparticles (Fig. 5) were used instead of Pt-black, the activation energy was slightly higher at lower coverage (Fig. 6). The reasons for the difference between data in Figs. 2 and 6 are at present unknown. What is known, however, is that the value of the diffusion coefficient is particle size dependent: between the 2.6 and ca. 7 nm samples, the coefficient at the near full coverage of CO<sub>ad</sub> is smaller by a factor of 4 for the 2.6 nm particles than for Pt-black, and by an order of magnitude smaller at nearly 0.5 coverage (Table 2).

<sup>&</sup>lt;sup>1</sup> Data for C-supported Pt 3.1 nm particles are similar to 2.6 nm.





Fig. 5. (a) TEM image and (b) histogram of particle size distribution for carbonsupported Pt nanoparticles (see Section 2).



Fig. 6. Variation of the diffusion coefficients with temperature for different CO
coverages, $\theta$ , on C-supported Pt 2.6 nm nanoparticles (the Arrhenius plots).
Black symbols: CO coverage corresponds to fully CO covered samples. Purple
symbols: CO coverage corresponds to partially covered samples. (For interpre-
tation of the references to color in this figure legend, the reader is referred to the
web version of the article.)

Table 2
CO diffusion parameters

Sample	$\theta^{\mathrm{a}}$	$E_d$ (kcal mol <sup>-1</sup> )	$D_{\rm CO}^0  ({\rm cm}^2  {\rm s}^{-1})$	$D_{\rm CO} \ ({\rm cm}^2  {\rm s}^{-1})$
		(kearmor)		
Dt/C(2.6 nm)	1.0	6.8	$1.0  imes 10^{-8}$	$9.1 \times 10^{-14}$
FUC (2.0 mm)	0.54	7.3	$1.8  imes 10^{-8}$	$7.2  imes 10^{-14}$
	1.0	6.0	$1.1  imes 10^{-8}$	$3.6  imes 10^{-13}$
Pt-black (7 nm)	0.68	6.7	$4.8 \times 10^{-8}$	$8.1 \times 10^{-13}$
	0.46	8.0	$8.8  imes 10^{-7}$	$9.5  imes 10^{-13}$
Unsupported Pt/Ru; 50:50 (2.7 nm)	~1.0	4.8	$1.0 \times 10^{-9}$	$2.8\times10^{-13}$

 $D_{CO}$ : the diffusion coefficient measured at 293 K.

<sup>a</sup>  $\theta_{CO}$  was estimated from CO oxidation charge obtained from cyclic voltammetry, with respect to hydrogen adsorption.

We can now use the relationship between the root mean square displacement ( $\Delta$ ) and CO diffusion coefficients obtained in this study  $D_{\rm CO}$ :  $\Delta = (4D_{\rm CO}t)^{1/2}$  [34] to calculate the displacement,  $\Delta$  (in nm), for CO surface diffusion (Table 3). The range of turnover rate,  $10^{-2}$  to  $10^{-3}$  molecule site<sup>-1</sup> s<sup>-1</sup> [53,54] are used as the reactivity benchmark when examining the importance of CO diffusion in the methanol oxidation process. Clearly, the root mean square displacement obtained show that CO diffusion is fast enough for CO to move around an entire Pt nanoparticle in ca. 1 s (Table 3), significantly exceeding that required for the turnover rates observed [53,54] (which indicate that one CO<sub>ad</sub> species is oxidized to  $CO_2$  at a single Pt site per 100 s, or longer).

As noted above, the Pt nanoparticle data are representative of DMFC catalysts at very low Ru coverage. However, preliminary data obtained with Pt/Ru nanoparticle catalyst show surface diffusion rates higher than that with pure platinum (Tables 2 and 3). Therefore, for such a low turnover rate for methanol oxidation, we conclude that these fast CO surface motions are unlikely to be the rate-limiting factors for methanol oxidation rates on Pt/Ru DMFC fuel cell anodes, although clearly CO surface diffusion experiments in a Nafion environment will be needed to test this hypothesis, and are planned for the immediate future.

We have also investigated E<sub>f</sub>-LDOS of the  $2\pi^*$  molecular orbital of adsorbed CO using the two-band model for CO chemisorption on platinum [23]. We find that the  $E_{f}$ -LDOS is correlated to the activation energy for diffusion (Table 4); the higher E<sub>f</sub>-LDOS, the higher the activation energy. More importantly, we find that the  $2\pi^*$  E<sub>f</sub>-LDOS for CO adsorbed

Table 3

CO diffusion parameters on several samples: fast CO surface motions (fourth column)

Sample	θ	$D_{\rm CO} ({\rm cm}^2{\rm s}^{-1})$	$\Delta'$ (for 1 s in nm) <sup>a</sup>
Pt/C (2 ()	1.0	$9.1  imes 10^{-14}$	6.0
Pt/C (2.6  nm)	0.54	$7.2  imes 10^{-14}$	5.4
	1.0	$3.6 \times 10^{-13}$	12
Pt-black (7 nm)	0.68	$8.1 \times 10^{-13}$	18
	0.46	$9.5 \times 10^{-13}$	19
Unsupported PtRu; 50:50 [22]	1.0	$2.8 \times 10^{-13}$	11

<sup>a</sup> The displacement in nm calculated for 1 s from the formula:  $\Delta = (4D_{\rm CO}t)^{1/2}$ , see [34].

ole 4

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LDOS of  $2\pi^*$  of adsorbed CO as a function of particle composition

nple	$E_{f}$ -LDOS ( $Ry^{-1}$ atom <sup>-1</sup> )	$E_{\rm d}  (\rm k cal  mol^{-1})$
supported Pt/Ru (50:50) black -black	$\begin{array}{l} 4.6 \pm 0.1^{a} \\ 7.0 \pm 0.2^{a} \\ 3.9 \pm 0.2^{b} \end{array}$	4.8 6.0 4.1 <sup>b</sup>

Ref. [19]. Ref. [7].

Iter. [7].

50:50 Pt/Ru nanoparticles (see Section 2) is nearly the same that of pure Ru-black, the observation that will have to be terrogated further.

#### Conclusions

We studied the surface diffusion of CO adsorbed on platum and on Pt/Ru nanoparticles by using <sup>13</sup>C electrochemical clear magnetic resonance spectroscopy in the temperature nge 253–293 K. We obtained new CO surface diffusion data th C-supported small Pt and Pt/Ru nanoparticle catalysts, and viewed [8,9] previous data obtained with Pt-black. On all noparticle surfaces investigated, we conclude that CO surface ffusion is too fast to be considered as the rate-limiting facr in methanol reactivity on DMFC catalysts. Further [8,9], we ve found that CO<sub>ad</sub> diffusion coefficients for the Pt-black sames follow Arrhenius behavior and that the diffusion parameters ow coverage dependence. For partially covered samples, the tivation energy increases linearly while the pre-exponential ctor increases exponentially, with decreasing coverage. This ggests that CO coverage is a significant factor in determing the diffusion rates. On Pt-black, although  $E_d$  increases with creasing coverage, the exponential increase in  $D_{CO}^0$ , due to e availability of more free surface sites, leads to a larger D<sub>ad</sub> diffusion coefficient at lower coverage. On C-supported noparticles, the  $E_{d}$ -coverage relationship is the opposite of at found on Pt-black, but the reasons for this behavior are t yet clear. Overall, these results, indicate that both partie size as well as coverage dependence need to be considered nen investigating surface reactions involving diffusive motions adsorbates during the elementary steps in fuel cell activity, d should therefore be included in surface electrochemical rate odeling calculations.

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