# Diffusion on a nanoparticle surface as revealed by electrochemical NMR

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Surface diffusion of chemisorbed CO (from MeOH electrochemisorption) on pure and Rumodified nanoscale Pt electrocatalyst surfaces has been investigated by solid-state electrochemical NMR (EC-NMR) in the presence of supporting electrolyte. Temperaturedependent nuclear spin-spin and spin-lattice relaxation measurements enable the diffusion activation energy, E, to be deduced. It is shown that the activation energy E correlates with the steady state current for MeOH electro-oxidation. A simple two-dimensional collision theory model is proposed to explain this intriguing observation, which may provide new mechanistic insights into the promotion of CO-tolerance in Pt/Ru fuel cell catalysts.

# Introduction

Surface diffusion of chemisorbed CO is one of the elementary steps of its catalytic oxidation on transition metal surfaces.<sup>1</sup> It is, therefore, of fundamental importance to achieve a detailed mechanistic understanding of how the diffusional behavior of CO can be tailored by chemical modifications of catalyst surfaces in order to increase catalytic reactivity. This is particularly important in electrochemistry-based fuel cell science since an efficient electro-oxidation of the chemisorbed CO, a potent surface poison of a platinum surface, is essential for any viable practical applications of fuel cells in providing future alternative clean energy sources.<sup>2,3</sup> Specifically, chemisorbed CO is a reaction intermediate in a direct methanol oxidation fuel cell (DMFC), generated *via* the reaction<sup>4</sup>

$$Pt + CH_3OH \rightarrow Pt-CO + 4H^+ + 4e^-$$
(1)

These strongly bound CO quickly block most of the active sites needed for a continuous electrooxidation of methanol to carbon dioxides. Even in the hydrogen fuel cell in which CO is not a reaction intermediate, the inevitable trace amount of CO contained in the hydrogen reformate, however, will still gradually passivate the Pt anode and eventually shut down the fuel cell. The current remedy for this problem is to intermix other metal elements with Pt by which the CO tolerance of the catalyst may be enhanced. Apparently, ruthenium appears to be one of the most promising promoters for CO oxidation to  $CO_2$ , *via* a so-called bifunctional mechanism:<sup>5</sup>

$$Pt-CO + Ru-OH \xrightarrow{\kappa} Pt + Ru + CO_2 + H^+ + e^-$$
(2)

where OH symbolizes the oxygen-containing species and k is the reaction rate constant.

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While eqn. (2) appears to be quite simple and intuitively straightforward, many details concerning the electronic, theoretical and surface motion aspects of this mechanism are, however, not well understood. The traditional interpretation of the bifunctional mechanism<sup>4,5</sup> is based on the fact that the more oxyphilic metal Ru can generate oxygen-containing species at much lower electrode potentials than does Pt, therefore, the presence of Ru substantially lowers the electrode potential at which the poisonous CO can be oxidized, eqn. (2). However, while this traditional view of the bifunctional or chemical mechanism highlights the fact that Ru is capable of generating oxygen-containing species at lower potentials than does Pt, it largely ignores the potentially critical electronic effects caused by alloying Ru to Pt, which can be expected to strongly influence metalligand bonding and, therefore, surface ligand diffusion. Since it is generally believed that the electro-oxidation of adsorbed CO follows the Langmuir–Hinshelwood mechanism, in which activated oxygen-containing surface species are involved, any effect of Ru on the surface diffusion of chemisorbed CO may play an important role in facilitating the reaction shown in eqn. (2).

In this paper we are concerned with the EC-NMR measurements<sup>6</sup> of the activation energy of the chemisorbed CO (from MeOH) surface diffusion on pure and Ru-modified nanoscale Pt electrode surfaces and the possible correlation between the surface diffusion and the enhancement in reactivity.

# Surface diffusion and NMR measurements

The NMR accessibility to diffusional information of species containing NMR active nuclei lies in the fact that two major NMR observables of dynamics, the nuclear spin-spin and spin-lattice relaxation processes characterized by relaxation times  $T_2$  and  $T_1$ , are intimately related to the microscopic motion of the species.<sup>7,8</sup> Surface diffusion modulates the local magnetic field as seen by the moving nuclear spins. These local field modulations, or fluctuations, then cause *irreversible* dephasing (*i.e.*, a  $T_2$  process) of the processing nuclear spins tilted by a  $\pi/2$  radio frequency (rf) pulse into a plane perpendicular to the external magnetic field  $H_0$  and stimulate quantum transitions (*i.e.*, a  $T_1$  process) between nuclear Zeeman levels which define the Larmor frequency.

If the fluctuations of the local field due to surface diffusion (*i.e.*, changes in magnitude and direction) are truly random, then any resemblance, or correlation, between local fields at time 0 and t, as seen by the nuclear spin, can be expressed by an autocorrelation function  $G(t)^7$ 

$$G(t) \propto \exp(-t/\tau_c)$$
 (3)

which is independent of the time origin. Here  $\tau_c$  is the correlation time for the motion (*e.g.*, the average time for CO jumping from one site to the other). The statistical meaning of the auto-correlation function is that it says that the probability of no local field fluctuation within a time interval *t* decreases exponentially as *t* increases.

Let us look at the  $T_2$  process first. Suppose that  $\Delta \omega$  is the amplitude of the local field fluctuation responsible for relaxation. Therefore,  $1/\Delta \omega$  defines the time needed for a complete dephasing. When  $\tau_c \gg 1/\Delta \omega$ , any single field fluctuation would dephase all the spin coherence before the next field fluctuation. This is the so-called "strong collision" limit and  $1/T_2 = 1/\tau_c$ . In contrast, when  $\tau_c \ll 1/\Delta \omega$ , no sufficient dephasing can build up between consecutive jumps and many random jumps are needed in order to achieve a complete dephasing. This is the so-called "weak collision" or "motion narrowing" limit and  $1/T_2 = (\Delta \omega)^2 \tau_c$ . In summary, for these two limiting cases one has:

$$1/T_2 = 1/\tau_c \text{ when } \tau_c \gg 1/\Delta\omega,$$
 (4)

and

$$1/T_2 = (\Delta \omega)^2 \tau_c \text{ when } \tau_c \ll 1/\Delta \omega.$$
(5)

In between,

$$1/T_2 = (\Delta\omega)^2 \tau_{\rm c} / (1 + (\Delta\omega)^2 \tau_{\rm c}^2)$$
(6)

which satisfies both limiting cases.

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For the spin-lattice  $T_1$  process, the most effective stimulating component of local field fluctuations that induces transitions between nuclear Zeeman levels is the one whose frequency equals the nuclear Larmor frequency. The Fourier transform of the autocorrelation function, eqn. (3), gives the amplitude of stimulation in terms of frequency so the spin-lattice relaxation rate due to the motion can be written as<sup>8</sup>

$$1/T_1 = 2(\delta\omega)^2 \tau_c / (1 + (\omega_0)^2 \tau_c^2)$$
<sup>(7)</sup>

where  $\omega_0$  is the Larmor frequency and  $\delta\omega$  the average difference in local field as seen by the nuclear spin during each molecular jump of which the average jumping time is  $\tau_c$ .

Assuming CO surface diffusion to be an activated motion, then  $\tau_c = \tau_{c0} \exp(E/k_B T)$ , where  $\tau_{c0}$  is a pre-exponential factor chosen to be  $10^{-13}$  s, and *E* is the activation energy for surface diffusion. It is clear that temperature-dependent spin–spin and spin–lattice relaxation measurements within the right temperature range will enable the activation energy *E* to be determined.

# Experimental

The starting batch of material for preparing Ru-modified Pt electrocatalysts was the commercial fuel cell grade (Johnson-Matthey, *ca.* 10 nm or 20 m<sup>2</sup> g<sup>-1</sup>). Ru was deposited onto Pt surfaces by the method of spontaneous deposition from an aqueous solution of RuCl<sub>3</sub>.<sup>9</sup> The packing density of ruthenium (the ratio of the number of Ru atoms to the number of Pt surface atoms) was estimated by inductively coupled plasma spectroscopy and cyclic voltammetry. Four Pt/Ru samples, having packing densities of 0, 0.14, 0.35, and 0.52, were so prepared and studied. They will be referred to as Pt/Ru-0 (*i.e.*, pure Pt), Pt/Ru-14, Pt/Ru-35, and Pt/Ru-52, respectively. The steady-state oxidation current, measured at 10 h after the reaction started and at a potential of 0.3 V *vs.* a reversible hydrogen electrode (RHE) in a supporting electrolyte of 0.5 M H<sub>2</sub>SO<sub>4</sub>, was found to be 0.035, 0.27, 0.74, and 0.75  $\mu$ A cm<sup>-2</sup> for Pt/Ru-0, -14, -35, and -52 respectively,<sup>10</sup> which represents an enhancement of *ca.* 20 times in reactivity.

For NMR measurements, about 500 mg Pt/Ru nanoparticles was first electrochemically cleaned in a conventional three-electrode cell and <sup>13</sup>C (99%) enriched methanol was then introduced into the cell at 0.19 V vs. RHE. After 12 h adsorption, excess methanol was removed by rinsing with 0.5 M D<sub>2</sub>SO<sub>4</sub> electrolyte, and the catalysts were transferred into pre-cleaned NMR ampoules, together with a small portion of electrolyte, and immediately flame-sealed. After such prolonged adsorption, the saturation CO packing on the surface, as obtained from CO stripping voltammetry,<sup>10</sup> was *ca*. 0.9 CO per metal surface site, indicating that CO is adsorbed not only on platinum but also on ruthenium.

All <sup>13</sup>C NMR measurements were carried out on an 8.47 T "homebuilt" NMR spectrometer, which consists of a (89 mm) widebore 8.47 T superconducting magnet (Oxford Instruments, Osney Mead, Oxford, UK), a Tecmag (Houston, Texas) Aries pulse programmer plus a variety of other digital and radiofrequency circuitries, and a "home-built" solenoidal NMR probe, housed in an Oxford Instruments CF-1200 cryostat. A Hahn spin-echo pulse sequence ( $\pi/2-\tau_0-\pi-\tau_0$ -acquisition) with a 16-step phase cycling to eliminate ringdown was used for data acquisition. For spin-spin relaxation measurements, the decay in the <sup>13</sup>CO NMR amplitude was monitored as a function of  $\tau_0$ ; and for spin-lattice relaxation measurements, an inversion-recovery method was used, which consisted of a preparative composite  $\pi$  pulse, ( $\pi/2$ )<sub>x</sub>( $3\pi/2$ )<sub>y</sub>( $\pi/2$ )<sub>x</sub>, followed by the aforementioned Hahn-echo acquisition sequence, with  $\tau_0$  set to either 30 or 35 µs. The  $\pi/2$  pulse length was typically between 5 and 8 µs, depending on experimental details.

# CO diffusion on pure Pt nanoparticles: Spin-spin relaxation measurements

Fig. 1A shows the <sup>13</sup>CO NMR spectrum and the temperature-dependent spin-lattice relaxation data of CO adsorbed on pure platinum nanoparticles (*i.e.*, Pt/Ru-0 sample). The spectrum can be represented by a single Gaussian and the straight line passing through the origin demonstrates the so-called Korringa relationship,<sup>11</sup> a NMR fingerprint of a metallic state, showing no evidence of other relaxation mechanisms than that by conduction electrons within the temperature range of the measurements. However, results for the temperature dependence of  $1/T_2$ , Fig. 1B, appear to be



**Fig. 1** <sup>13</sup>CO NMR data of CO on a Pt/Ru-0 (pure Pt) sample: A The NMR spectrum and the Korringa relationship which indicates a metallic state and B, the temperature-dependent spin-spin relaxation rate  $(1/T_2)$  data. The solid line in B is the fit to eqn. (8).

more complex. In fact, for CO adsorbed onto small platinum particles, several relaxation mechanisms for  $1/T_2$  are active:<sup>6</sup> the temperature independent "rigid lattice" contribution  $1/T_2^{\text{RL}}$ , the  ${}^{13}\text{C}{-}^{195}\text{Pt}$  scalar contribution  $1/T_2^{\text{Pt}}$ , the  ${}^{13}\text{C}{-}^{13}\text{C}$  dipole–dipole contribution  $1/T_2^{\text{dip}}$ , and the local field inhomogeneity contribution  $1/T_2^{\text{diff}}$ . Specifically,  $1/T_2^{\text{Pt}}$  arises from the field fluctuation caused by spin-flipping of Pt that forms a

Specifically,  $1/T_2^{\text{Pt}}$  arises from the field fluctuation caused by spin-flipping of Pt that forms a bond with CO. The rate of fluctuation is determined by its spin-lattice relaxation, which follows the Korringa relation  $T_1T$  = constant where T is the absolute temperature. It is believed that within the temperature range shown in Fig. 1B this mechanism is in the strong collision limit.<sup>12</sup> Therefore,  $1/T_2^{\text{Pt}} = aT$ , with a being a constant.  $1/T_2^{\text{dip}}$  is due to dipolar interactions between neighboring <sup>13</sup>C spins. Since the peak disappears when the <sup>13</sup>C nuclei are isotopically diluted, <sup>13</sup> one can safely attribute it to dipolar interactions, which indicates that a transition from the strong to weak collision limit is being observed for the dipolar contribution. So  $1/T_2^{\text{dip}} = (\Delta\omega)^2 \tau_c/(1 + (\Delta\omega)^2 \tau_c^2)$ , with  $\Delta\omega$  representing the strength of the dipolar field. Finally, the field fluctuation for  $1/T_2^{\text{diff}}$  comes from the presence of a significant static magnetic field inhomogeneity on the particle surface. Thus, when a CO diffuses randomly on the surface, it sees the changes in both the orientation and the magnitude of the field after each jump, which effectively generates a dynamic modulation to irreversibly dephase the spin coherence. Assuming N jumps are needed for dephasing about 1 rad, then  $1/T_2^{\text{diff}} = 1/N\tau_c$ . In summary:

$$1/T_2 = 1/T_2^{\text{RL}} + 1/T_2^{\text{Pt}} + 1/T_2^{\text{dip}} + 1/T_2^{\text{diff}} = 1/T_2^{\text{RL}} + aT + (\Delta\omega)^2 \tau_c / (1 + (\Delta\omega)^2 \tau_c^2) + 1/(N\tau_c)$$
(8)

The solid line in Fig. 1B is the fit to this equation with  $1/T_2^{\text{RL}}$ ,  $a, \Delta \omega, E$ , and N as fitting parameters. The results of the fits are:  $1/T_2^{\text{RL}} = 293 \text{ s}^{-1}$ ,  $a = 5.4 \text{ s}^{-1} \text{ K}^{-1}$ ,  $\Delta \omega/2\pi = 1.1 \text{ kHz}$ ,  $E = 7.8 \text{ kcal mol}^{-1}$ , and N = 977. Notice that the activation energy found for CO, 7.8 kcal mol<sup>-1</sup>, is quite close to that found for CO on "dry" alumina-supported Pt clusters,<sup>14</sup> as well as to that found in single crystal studies.<sup>1</sup>

# CO diffusion on Ru-modified Pt nanoparticles: Spin-lattice relaxation measurements

We show in Figs. 2 and 3 <sup>13</sup>CO EC-NMR results for the Pt/Ru-14, 35, and -52 catalyst samples. The normalized <sup>13</sup>C NMR spectra shows clearly a new NMR feature, appearing at the highfield side (lower ppm value) of the spectra, whose intensity increases as the Ru content increases, Fig. 2

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Fig. 2  $^{13}$ CO NMR spectra of CO chemisorbed on Ru-modified Pt samples. The dashed spectrum is reproduced from Fig. 1A for comparison. As the Ru packing density increases, the amplitude of the new spectral feature appearing at the highfield side also increases.

(the dashed spectrum is the one already shown in Fig. 1A but is reproduced here for comparison). Since both the electrochemical cyclic voltammogram results<sup>9,10</sup> and theoretical modeling<sup>15</sup> suggest the existence of two CO domains, the <sup>13</sup>C NMR spectra in Fig. 2 were thus simulated by using two Gaussians and the results are shown in the insets in Fig. 3A–C. The fractions of the CO molecules on Pt/Ru sites (represented by the highfield Gaussian) obtained from the <sup>13</sup>C NMR spectral deconvolutions were 0.28, 0.54, and 0.63, for Pt/Ru-14, -35, and -52, respectively.

Also shown in Fig. 3 are the temperature-dependent spin-lattice relaxation rate  $(1/T_1)$  results measured at the spectral positions indicated in the insets, which indeed corroborate well with the assumption of two CO domains. As clearly seen, the CO domain represented by the lowfield Gaussian (at high ppm value) shows only the Korringa relaxation mechanism (*i.e.*, by conduction electron) for all three Ru-modified samples, similar to that observed on the pure Pt sample (Fig. 1A). However, the CO domain represented by the highfield Gaussian behaves quite differently: while at lower temperature (<200 K) the relaxation is still predominantly caused by the conduction electrons, as indicated by the straight lines passing through the origin, major deviations from such a simple Korringa relationship are observed at higher temperatures. These deviations clearly indicate the onset of a second relaxation mechanism. The solid curves in Fig. 3C and D are the fits to eqn. (9), which take into account this thermally activated process, presumably surface diffusion:

$$T^{1} = aT + 2(\delta\omega)^{2}\tau_{c}/(1+\omega_{0}^{2}\tau_{c}^{2})$$
(9)

where the first term is the standard Korringa contribution in which T is the absolute temperature and  $a^{-1}$  is the Korringa constant, obtained from the straight-line fit at T < 200K. The second term is the same as eqn. (7) and accounts for the surface diffusion. The fit gives two parameters: the average local field inhomogeneity felt by a molecule during each jump ( $\delta\omega$ ) and the activation energy for diffusion (E). The values obtained for  $\delta\omega/2\pi$  and E are 3.3, 2.7, and 3.6 kHz and 5.7, 4.9, and 5.1 kcal mol<sup>-1</sup>, for Pt/Ru-14, -35, and -52, respectively. Notice that the activation energy for CO diffusion on pure Pt under the same electrochemical conditions is 7.8 kcal mol<sup>-1</sup> (*vide supra*). Clearly, the presence of Ru substantially enhances surface diffusion for the CO molecules on Pt/Ru sites, but for the Pt sites, the effects are quite small since over the same temperature range only the pure Korringa mechanism was observed there. Notice also that since the local field inhomogeneity



Fig. 3 <sup>13</sup>CO NMR spectral deconvolution and the temperature-dependent spin-lattice relaxation  $(1/T_1)$  data for Ru-modified Pt samples. The different relaxation behaviors discernible by <sup>13</sup>CO NMR at the high- and low-field sides indicate the existence of two subsets of CO molecules and the exchange (diffusion) between them is rather slow on the NMR timescale.

 $\delta\omega/2\pi$  is 3 times larger than the <sup>13</sup>C–<sup>13</sup>C dipole–dipole interaction  $\Delta\omega/2\pi$ , any relaxations through mutual spin flips are effectively quenched.

# Correlation between the surface diffusion and the reactivity: A simple twodimensional collision theory model

Without resorting to any detailed theoretical model, the mere fact that CO molecules resonating at high frequencies (on the left of the NMR spectra) obey the Korringa relationship over the entire experimental temperature range, while those resonating at low frequencies (on the right) show a diffusional contribution at higher temperatures (Fig. 3), indicates that at least two different populations of chemisorbed CO must exist on Pt/Ru surfaces. In one subset (CO molecules–Pt/Ru), diffusion is faster than in the other (CO molecules–Pt) and exchange (diffusion) between these two populations must be *slow* on the NMR timescale. Since Ru forms nanometer islands on the Pt surface and the ratios between the fraction of CO molecules–Pt/Ru and the Ru packing density: 2.0, 1.5, and 1.2 for Pt/Ru-14, 35, and -52 respectively, are all larger than unity, this (faster diffusion) subset must contain CO on Pt sites next to the peripheries of Ru islands, as illustrated by the cartoon in Fig. 4.

It is now interesting to see if there is any correlation between the NMR and catalytic activity results. As shown in Fig. 5, the steady-state methanol electro-oxidation currents (reactivity) at 10 h when plotted against the diffusion activation energy of CO molecules at the Pt/Ru sites (measured by <sup>13</sup>C NMR) result in an Arrhenius-type relationship. While based on only a small data set, the slope of the linear correlation (with an  $R^2 = 0.98$ ) of -1.1 mol kcal<sup>-1</sup> is remarkably close to the expected universal constant: -1/RT = -1.7 mol kcal<sup>-1</sup> (*vide infra*), where *R* is the gas constant and *T* is room temperature (298 K). Of course, methanol electro-oxidation on a catalyst surface is undoubtedly a very complex process. However, for methanol electro-oxidation the rate-limiting step, eqn. (2), is expected to follow the Langmuir–Hinshelwood or bifunctional mechanism and consequently can be modeled by using a two-dimensional collision theory.<sup>16</sup> In this case, the reaction rate can be expressed as:

$$k \propto v_{\rm r} \exp(-E_{\rm react}/RT)$$
 (10)

where  $v_r$  is the relative velocity between CO and OH, and  $E_{react}$  the energy barrier for the reaction. Since oxygen-containing species usually form a much stronger bond with the metal surface than

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Fig. 4 Cartoon to illustrate the two-CO-domain model.

CO and, under steady-state conditions, only CO molecules on the Pt side of the Pt/Ru edge are present and diffuse towards OH-covered Ru islands where they are oxidized (eqn. (2)), then, to a good approximation,  $v_r \propto \tau_c^{-1} = \tau_{c0}^{-1} \exp(-E/RT)$ . Thus, the reaction current  $j \propto k \propto \tau_{c0}^{-1} \exp(-E/RT) \exp(-E_{react}/RT)$ . Assuming  $E_{react}$  is more or less a constant, which appears to be the case,<sup>17,18</sup> then within the framework of this model, one would expect a linear correlation between  $\ln(j)$  and Eat room temperature, with a slope of -1/RT = -1.7 mol kcal<sup>-1</sup>. (Notice that this is a relationship at a *constant* temperature as a function of E.) This is indeed, to a good first approximation, exactly what we find in Fig. 5. While the difference in slope between -1.1 and -1.7 mol kcal<sup>-1</sup> might indicate the possible changes in  $E_{react}$ , this observation strongly suggests that eqn. (10) may still provide a reasonable mechanistic framework to interpret the basic bifunctional mechanism shown in eqn. (2).

# Conclusions

Three important conclusions can be drawn from the results shown above. (1) On Ru-modified Pt surface, two subsets of CO are discernible by EC-NMR: CO molecules on Ru islands and on Pt



**Fig. 5** Graph showing an Arrhenius relationship between the long-term (10 h) steady-state current and the diffusional activation energy for CO molecules on Pt/Ru sites at the catalyst surfaces. The  $R^2$  of the fit is 0.98. The slope of the straight line is -1.1 mol kcal<sup>-1</sup>, to be compared with -1.7 mol kcal<sup>-1</sup>, the universal constant -1/RT, at room temperature (298 K).

sites next to the peripheries of Ru islands that have a lower activation energy for diffusion than CO molecules on Pt sites distant from Ru. (2) The exchange (diffusion) between these two CO subsets is slow on the NMR timescale. (3) It is shown that there is a simple Arrhenius-type relationship between the long-term steady-state methanol electro-oxidation current and the diffusional activation energy of the CO molecules on Pt/Ru which can be reasonably explained by a simple two-dimensional collision theory model. Altogether, these results strongly indicate that, in addition to the conventional bi-functional mechanism, surface dynamic effects may play a much more important role in enhancing CO tolerance than previously thought—fast diffusion results in rapid elimination of the adsorbed CO poison.

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