Contents lists available at SciVerse ScienceDirect







journal homepage: www.elsevier.com/locate/electacta

Morphology-dependent activity of Pt nanocatalysts for ethanol oxidation in acidic media: Nanowires versus nanoparticles

Wei-Ping Zhou^{a,*}, Meng Li^a, Christopher Koenigsmann^b, Chao Ma^c, Stanislaus S. Wong^{b,c}, Radoslav R. Adzic^a

^a Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, United States

^b Department of Chemistry, State University of New York at Stony Brook, Stony Brook, NY 11794, United States

^c Condensed Matter Physics and Materials Sciences Department, Brookhaven National Laboratory, Building 480, Upton, NY 11973, United States

ARTICLE INFO

Article history: Received 12 May 2011 Received in revised form 16 August 2011 Accepted 16 August 2011 Available online 25 August 2011

Keywords: Fuel cell Heterogeneous catalysis Platinum Nanowires Ethanol oxidation

ABSTRACT

The morphology of nanostructured Pt catalysts is known to affect significantly the kinetics of various reactions. Herein, we report on a pronounced morphology effect in the electrooxidation of ethanol and carbon monoxide (CO) on Pt nanowires and nanoparticles in an acidic solution. The high resolution transmission electron microscopy analysis showed the inherent morphology difference between these two nanostructured catalysts. Voltammetric and chronoamperometric studies of the ethanol electrooxidation revealed that these nanowires had a higher catalytic activity by a factor of two relative to these nanoparticles. The rate for CO monolayer oxidation exhibits similar morphology-dependent behavior with a markedly enhanced rate on the Pt nanowires. *In situ* infrared reflection–absorption spectroscopy measurements revealed a different trend for chemisorbed CO formation and CO₂-to-acetic acid reaction product ratios on these two nanostructures. The morphology-induced change in catalytic activity and selectivity in ethanol electrocatalysis is discussed in detail.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Nanostructured Pt is one of the most widely studied electrocatalytic materials in energy related technologies, particularly in low-temperature fuel cells [1]. A fundamentally interesting feature of these nanostructured Pt catalysts is their size- and morphologydependent electrocatalytic activity [1–15]. The conventional Pt electrocatalysts with zero-dimensional (0-D) nanoparticle morphologies generally have large numbers of low coordination atoms (LCAs) and defects on their surfaces. By contrast, Koenigsmann et al. [14,16] have shown that the Pt nanostructures with ultrathin onedimensional (1-D) nanowire morphologies maintain elongated single crystalline segments with smooth crystal planes that are connected by grain boundaries forming a nanowire structural motif. Hence, these structures possess proportionally less surface LCAs as compared with their associated 0-D analogues [13-18]. Moreover, the electronic property of noble metal nanowires (Au, Pt, Pd) could be largely altered due to a surface contraction effect and a surface-stress-induced phase transformation, when their diameter decreased below a critical value of 2 nm [19–22]. The unique structural and electronic properties of Pt catalysts linked to 1-D morphologies could be largely responsible for their significantly enhanced catalytic performance in the oxygen reduction reaction (ORR) and methanol oxidation reaction (MOR), as demonstrated from our previous studies as well as those from other groups [13–15,17,18].

The structural effect on the Pt catalytic activity in the ethanol oxidation reaction (EOR) has been demonstrated from a number of studies on well-ordered [23-27] as well as nanostructured [2,8] surfaces. The role of the LCAs has been highlighted in these studies and these sites are generally regarded to favor C-C bond splitting [2,8,24–26]. However, ethanol oxidation is a complicated reaction and comprises multiple reaction steps that may maintain different structural sensitivity in each step. Although C-C bond splitting and OH adsorption for surface CO oxidation have been reported to be step site-favored reaction steps in the EOR [23–25,27], C-dehydrogenation is believed to be a predominantly terrace-favored reaction, as evidenced from the methanol oxidation reaction [25,28,29]. Therefore, the Pt nanostructures with a high density of surface LCAs may not necessarily lead to a high activity, given different site preferences associated with different reaction steps in the EOR. For example, Colmati et al. [25] suggested that the optimized performance of the Pt catalyst for the EOR can only be achieved with a balance between surface terrace and step sites. Additionally, it has also been demonstrated that the step sites with different symmetry and electronic property may have different reactivity and selectivity in the EOR [23-25,27]. Furthermore, nanostructured materials may exhibit catalytic behaviors

^{*} Corresponding author. Tel.: +1 631 3447298; fax: +1 631 3445815. *E-mail address:* wpzhou@bnl.gov (W.-P. Zhou).

^{0013-4686/\$ -} see front matter © 2011 Elsevier Ltd. All rights reserved. doi:10.1016/j.electacta.2011.08.055

significantly different from that of well-ordered surface studies. For example, CO monolayer oxidation is generally considered as a step site-favored reaction from well-ordered surface studies [23,29,30]. In fact, it has been reported by several other studies that smaller nanoparticles are less active than larger particles for CO monolayer oxidation, although the number of the LCAs is expected to increase progressively as the particle size is decreased [3,5,6]. It has been suggested that this size-dependent activity is due to stronger bonding of CO to smaller particles and hence a decrease in the surface diffusion rate [5,6]. To further explore the nanostructure-induced change in electrocatalytic activity, we have carried out ethanol and CO electrooxidation on Pt nanocatalysts with distinctively different morphologies.

In the present work, we used a combination of electrochemical methods, in situ infrared reflection-absorption spectroscopy (IRRAS), and high resolution transmission electron microscopy (HRTEM) to study ethanol oxidation on two nanostructured Pt catalysts, namely nanowires (NWs) and nanoparticles (NPs). Our ultra-thin Pt NWs ($d: 1.6 \pm 0.4$ nm) had larger crystalline facets and fewer surface LCAs as compared with commercial Pt catalysts composed of nanoparticles (d: 2.4 ± 0.4 nm) [14]. We found that the ultrathin Pt NWs exhibited a significantly lowered onset potential and also an increased faradic current with a factor of two to three as compared with the Pt nanoparticles in the EOR. In fact, the initial onset potential for the EOR on our ultrathin nanowires was approaching the one obtained on a state-of-the-art Pt/Sn bimetallic catalyst [31]. Our in situ IRRAS study provided mechanistic insight into this morphology-dependent activity and selectivity of the EOR. We demonstrated that the morphology of the nanostructured materials may have a more profound effect than anticipated from well-ordered surface studies on ethanol electrocatalysis.

2. Experimental

2.1. Preparation of nanostructured Pt nanowires

A Pt/C sample (46.4 wt.%) from Tanaka Kikinzoku (TKK) International Inc. was used as the Pt nanoparticle reference without further treatment. Details of ultra-thin Pt nanowire (NW) synthesis and characterization have been reported elsewhere [14]. In brief, a 2.5 mL aliquot of a hexachloroplatinic (IV) acid hydrate $(H_2PtCl_6 \cdot H_2O, >99.9\%, Aldrich)$ solution (10.0 mM, aqueous) was dissolved in a solvent system comprised of 20 mL dimethylformamide (EMD, anhydrous), 12.5 mL toluene (Acros, reagent grade), and 2.5 mL triethylamine (Fisher, reagent grade). The Pt precursor was reduced by the addition of 20 mg of sodium borohydride while stirring, and the reaction was allowed to proceed for 3 h. The resulting black product was precipitated by centrifugation and was further washed several times with either absolute methanol or ethanol. The isolated product was subsequently dispersed and treated in a solution of 6M HCl, sonicated, and washed several times with aliquots of water and ethanol. The morphology and dimensions of as-prepared Pt NWs were characterized using a transmission electron microscopy instrument (JEOL 3000, BNL). The average diameter of wires was 1.6 ± 0.4 nm with an average length of 100 ± 25 nm, as shown in Fig. 1c.

2.2. Electrochemical measurements

Preparing a thin film of catalysts on a glassy carbon electrode (5 mm diameter, Pine instrument) involved dispersing a certain amount of catalysts in water (in our case, 1 mg catalysts dispersed into 1 mL water) and sonicating for ca. 10 min to create a uniform suspension [32]. Then, 10 μ L of this suspension was placed onto a glassy carbon disk and dried in the air. The electrode was covered



Fig. 1. Voltammetric curves for (a) Pt nanowires and (b) Pt nanoparticles in 0.1 M HClO₄ solution. Scan rate: 50 mV s^{-1} . Currents are normalized to the measured Pt surface area (H_{ads} charge after double layer correction). Typical HRTEM images are highlighted of Pt nanowires (c) and Pt nanoparticles (d).

with 5 μ L of 4 μ g/10 μ L Nafion[®] solution (diluted with water from 5% Nafion solution by Aldrich) and dried again before the EOR and CO oxidation measurements.

For the CO (Matheson, 99.8%) adsorption and electrooxidation experiments, the saturated CO adlayer was formed in a CO saturated solution (holding at 0.05 V for 5 min) followed by purging of the electrolyte with Ar (20 min). Thus, the CO electrooxidation process was performed in a CO-free solution.

Ethanol (anhydrous, Reagent Grade) was purchased from Sigma-Aldrich and all solutions were made with Milli-Q water (Millipore, Bedford, MA). All potentials were measured using an Ag/AgCl (3 M Cl⁻) electrode (Bio), but reported with respect to a reversible hydrogen electrode (RHE). All electrochemical measurements were performed in a 0.1 M HClO₄ (Optima, Fisher) solution at room temperature. The selection of HClO₄ solution as the supporting electrolyte discards the possible anion effect in the catalytic process. All the electrochemical data are reported with the surface area normalized in terms of the electrochemical active surface area (ECSA) that was calculated using the charge density obtained from an integrated H adsorption peak after correcting for the double layer contribution and assuming a relationship of 210 μ C/cm²_{Pr}. All of the current densities reported here are normalized to the electrochemical active surface area of Pt so that the activity of different Pt catalysts tested can be directly compared.

2.3. In situ infrared reflection-absorption spectroscopy

In situ IRRAS studies were performed with a Nicolet Nexus 670 FT-IR spectrometer equipped with a MCT (Mercury-Cadmium-Telluride) detector cooled with liquid nitrogen. An unpolarized light beam was used. The spectral resolution was set to 8 cm⁻¹ and 128 interferograms were together added to each spectrum. Spectra are given in absorbance units defined as $A = -\log(R/R_0)$, where R and R_0 represent the reflected IR intensities corresponding to the sample- and reference-single beam spectrum, respectively. The reference spectrum was collected at 0.05 V in the same solution with 0.1 M ethanol and 0.1 M HClO₄. Band intensity and position were analyzed with the Omnic program. A ZnSe hemisphere was used as the IR window, and the working electrodes used in this IR study, including Pt NW and Pt NP electrocatalysts deposited on a polycrystalline Au disk, were pressed against the IR window to create a thin solution layer with a thickness of a few micrometers. Pure Ar and dry air were used to



Fig. 2. Comparison of voltammetric curves for the first scan (a) and the second scan (b) taken in the positive direction (solid line) and negative direction (dashed line) for Pt nanowires (black line) and nanoparticles (red line) after the sample was immersed in 0.2 M ethanol in 0.1 M HClO₄ solution at 0.07 V under potential control. Scan rate: 10 mV s^{-1} . Currents are normalized to the measured Pt surface area. Inset shows the comparison of the curves at the low current density region. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

purge the electrolyte and spectrometer, respectively, in order to remove the spectral interference from CO_2 and water vapor in air.

3. Results and discussion

Fig. 1 shows typical cyclic voltammetry (CV) scans of the Pt NWs and Pt NPs recorded in an argon-saturated 0.1 M HClO₄ solution at room temperature, together with representative, associated HRTEM images. The HRTEM image in Fig. 1c highlights the presence of well-defined individual nanowires with an average diameter of 1.6 ± 0.4 nm. Specifically, the nanowires consist of multiple crystalline segments with an average length of 6 ± 2 nm that extends along the axis of the nanowire (see Fig. 6) [14]. The average particle size of the Pt NPs is 2.4 ± 0.4 nm (Fig. 1d), which is slightly larger than the Pt NWs. For a close comparison of the electrochemical features of two Pt nanostructures, the catalyst surface area has been normalized to the Pt specific surface area. Current features at \sim 0.14V associated with (110)-type of defect sites are clearly observed on the Pt NPs but are almost indiscernible on the Pt NWs (Fig. 1a and b), suggesting considerably less LCAs on the nanowires [14]. In the surface hydroxyl formation region, the Pt NWs display a positively shifted onset of oxidation and also a suppressed intensity as compared with the Pt NPs, a clear indication of a weaker binding of OH species on the former. Our previous work [14] demonstrated that decreasing the binding of oxygen to Pt NWs leads to a significantly enhanced ORR activity as compared with the Pt NPs.

Fig. 2 shows CV scans of ethanol oxidation on the Pt NWs and Pt NPs in 0.2 M ethanol in 0.1 M HClO₄ solution at room temperature. The positive potential limit set at 0.92 V prevents possible perturbation of the Pt morphology during potential cycling to higher values. The ethanol oxidation experiments were always performed with immersion of the catalysts at 0.07 V under potential control where ethanol oxidation is negligible [33] and with subsequent scans in a positive-going direction. This method is very helpful for understanding the catalytic behavior of a Pt surface covered either with or without surface intermediates formed during CV scans. Fig. 2a

and b show and compare the first and second CV scans, respectively, of the Pt NWs and Pt NPs. Significant voltammetric changes were not observed after the second scan for both of the samples. However, there are several important features noted between these two samples during the first and second scans. In the first positivegoing scan, the Pt NPs evince a low activity with an onset potential at about 0.45 V (measured at $j = 0.01 \text{ mA cm}^{-2}$). However, the Pt NWs display significantly higher activity with an onset potential occurring at about ~0.23 V measured at the same current density, as well as a greater shift of \sim 0.22 V toward the negative direction as compared with the Pt NPs. This onset potential shift on the ethanol oxidation is approaching that obtained for state-of-the-art bimetallic catalysts. In fact, a 0.25 V negatively shifted onset potential has been reported on Pt₃Sn/C when compared with Pt/C [31]. Moreover, our nanowires also demonstrated an increased current density, about 2-3 times higher relative to that of nanoparticles in the potential range of 0.20-0.92 V in both the positive and negative scan directions. A similar activity enhancement for ethanol oxidation on Pd 1-D nanostructures as compared with their associated 0-D counterparts has also been reported [17].

Subsequent CV scans recorded on both nanoscale electrocatalysts show noteworthy differences, including a positively shifted onset potential and a decreased current density as compared with the first CV scan. The Pt NWs still display a considerably lower onset potential (\sim 0.48 V at j = 0.01 mA cm⁻²) as compared with the Pt NPs (~0.59V) in the second positive-going scan. Moreover, the Pt NWs demonstrated a lower current decrease relative to the Pt NPs, e.g. \sim 5% on NWs versus \sim 15% on NPs at peak potential (0.88 V here). A similar activity loss in consecutive scans of Pt catalysts in ethanol solution has been reported elsewhere [33,34]. Previous in situ FTIR experiments [33,34] as well as recent sum-frequency generation (SFG) studies [35] show that the CO are accumulated on the surface during the first negative-going scan and attained the highest coverage when the electrode reached the negative most potential of the scan window (0.07 V in this case). In addition, results from those spectroscopy studies as well as differential electrochemical mass spectrometry (DEMS) [26,36] and surface enhanced Raman



Fig. 3. Comparison of current-time plots for ethanol oxidation activity on Pt nanowires (black) and nanoparticles (red) in 0.2 M ethanol in 0.1 M HClO₄ solution at 0.65 V for 3600 s reaction time. Inset shows comparison of current densities measured at three different potentials (0.55 V, 0.60 V and 0.65 V) at 500 s reaction time. All current data were recorded after the catalysts were immersed at 0.07 V under potential control and then stepped to reaction potentials. Currents are normalized to the measured Pt surface area. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

spectroscopy (SERS) [37] measurements indicate the difficulty in the electrooxidation of $-CH_x$ species at low potentials, which may also lead to the accumulation of $-CH_x$ adsorbates on the surface at potentials near the onset of ethanol oxidation. Therefore, the decreased activity of Pt catalysts in a subsequent positive-going CV scan can be ascribed to the poisoning effect of both adsorbed CO and -CH_x surface species mutually formed in the preceding negativegoing scan. It is unlikely that the adsorption of acetic acid played a significant role in the onset potential shift, given its particularly low concentration at the interface at low potentials near the onset of ethanol oxidation and the similar adsorption strength to that of the (bi)sulfate that does not show such a significant effect upon the onset potential shift [25,35]. Regardless, the Pt NWs still exhibit better catalytic performance, i.e. higher currents and lower onset potentials, as compared with the Pt NPs, despite the partially covered surface by adsorbed CO and -CH_x species. This significantly enhanced catalytic performance noted with nanowires highlights the inherent advantages of using 1-D nanostructures in ethanol electrocatalysis.

Chronoamperometric (CA) measurements have been performed to test the activity and stability of these two Pt catalysts, as shown in Fig. 3. The CA data were recorded after the catalysts had been immersed at 0.07 V under potential control and then stepped to 0.6 V. Clearly, the Pt NWs display higher current density, that is, higher activity, both at the experimental beginning and also, after 3600 s of reaction at 0.6 V. The activity loss is significantly different for both catalysts. That is, it takes about 1000 and 60s of reaction time for the Pt NWs and Pt NPs, respectively, to lose 50% of their initial activity. After 3600s of reaction, the Pt NWs still displayed an outstanding activity with a measured current density of 0.076 mA cm⁻², which was about 2-fold higher than that of Pt NPs (0.036 mA cm⁻²). The ethanol oxidation at three different potentials (e.g., 0.55 V, 0.60 V, and 0.65 V) at 500 s of reaction shows a consistently enhanced activity for the Pt NWs, i.e. slightly varied at about 3-fold enhancement, as compared with the Pt NPs (inset



Fig. 4. In situ IRRAS spectra recorded during ethanol electrooxidation on Pt nanoparticles (a) and Pt nanowires (b) in a 0.2 M ethanol in 0.1 M HClO₄ solution. 128 interferograms (resolution of 8 cm⁻¹) were collected and added into each spectrum.

in Fig. 3). The CA data again confirmed the significantly enhanced catalytic performance on 1-D nanostructures seen in our complementary potentiodynamic measurements. However, mechanisms for the current decay still remain unclear and further investigation is expected to give insight into the enhanced stability of the 1D Pt.

To shed light upon this morphology-induced activity change in ethanol oxidation, *in situ* IRRAS studies were carried out to verify surface intermediate formation and product distribution on both Pt catalysts. Fig. 4 displays the recorded spectra and Table 1 lists the associated frequencies and band assignments. Carbon monoxide (CO), carbon dioxide (CO₂), and acetic acid (CH₃COOH) are the main species observed on both Pt catalysts. The band at around 2030 cm^{-1} can be assigned to a linear bound CO_{ads}, an indication of C–C bond cleavage in ethanol molecules. However, chemisorbed surface CO_{ads} is also a catalytically poisoning intermediate that

Table		1		
	•	IDD		

In situ IRRAs spectra band assignments.

Wavenumber/cm ⁻¹	Assignment
2343	CO ₂ asymmetric stretching
2030	CO linear bonding
1705	C=O stretching of CH ₃ CHO and CH ₃ COOH in solution
1620-1635	C=O stretching of adsorbed acetaldehyde and acetyl
$\sim \! 1598$	H-O-H deformation of adsorbed water
1396-1410	O-C-O stretching of adsorbed acetate
~ 1350	CH plane bending of adsorbed acetate
1280	C–O stretching of CH ₃ COOH in solution
1368	CH ₃ symmetric deformation and C-H wagging in CH ₃ CHO



Fig. 5. (a) Integrated band intensities of linear band CO_{ads} (2030 cm⁻¹) as a function of electrode potential in IRRAS spectra recorded in a positive scan-direction during ethanol oxidation on Pt nanowires (bottom panel) and nanoparticles (upper panel). (b) The ratio of the integrated band intensity of CO₂ (2343 cm⁻¹) with respect to CH₃COOH (1280 cm⁻¹) plotted as a function of applied electrode potential.

impedes further ethanol oxidation on Pt. The positive-going peak near 2343 cm⁻¹ is attributed to the asymmetric stretch vibration of CO_2 , which is the product of the ethanol total oxidation pathway. The band located around 1705 cm⁻¹ can be ascribed to the stretching vibration of the C=O bond in both acetaldehyde and acetic acid, and the appearance of this band indicates partial oxidation of ethanol. The band at 1280 cm⁻¹ is the characteristic C–O stretching vibration of acetic acid, which can be used for quantitative analysis of acetic acid formation [27,38].

Evolution of the CO_{ads} band and CO₂-to-CH₃COOH ratios on two nanostructures has been checked. Fig. 5a shows integrated band intensities of the linear CO_{ads} band at 2030 cm⁻¹, plotted against electrode potentials, formed in a positive scan-direction on the Pt NWs and NPs. In Fig. 5b, we plotted as a function of electrode potential the ratio of integrated band intensities between the CO₂ band (2343 cm^{-1}) and the CH₃COOH band (1280 cm^{-1}) . The high ratio represents the catalysts' high efficiency in the complete oxidation of ethanol to CO₂. The potential dependence of CO_{ads} evolution on the Pt NPs is consistent with previous studies on carbon-supported Pt catalysts with similar particle sizes [39]. While the Pt NWs exhibit a very similar CO_{ads} evolution profile to that of Pt NPs, there are several distinctive differences between the two nanostructures. First, we observed that the onset potential of the CO_{ads} band on the Pt NPs is slightly below 0.3 V and is lower than that on Pt NWs (0.3 V), probably because of the high density of step and edge sites on nanoparticles that are favored in C–C bond splitting [2,8,25,26]. Second, we found that the CO_{ads} band begins to decrease at 0.45 V on the Pt NWs but at 0.62 V on the Pt NPs, coincident with the appearance of CO oxidation features in the pre-ignition potential region shown in the voltammetric curve (see discussion below in Fig. 6). The significant negative-potential shift (\sim 0.17 V) in CO_{ads} oxidation suggests an efficient removal of surface chemisorbed CO formed on the Pt nanowires. In addition, the Pt NWs displayed a slightly increased CO₂-to-CH₃COOH reaction product ratio relative to that of the Pt NPs at potentials below 0.60 V where the presence of CO_{ads} was predominantly observed for both catalysts. A similar ratio was seen in the potential range of 0.6-0.8 V where CO oxidation can occur on nanoparticles. However, when the surface CO was significantly lower at high potentials (>0.8 V), the Pt NWs again displayed a greatly increased CO₂-to-CH₃COOH ratio. This observation may have been caused by a significant oxidation of Pt nanoparticles in this particular potential range, thereby preventing effective ethanol oxidation.

Since oxidation of the surface CO_{ads} intermediate is a crucial step in a complete oxidation of ethanol to CO₂ [8,23,25,27,33,34,38], we further performed CO stripping experiments to explore this morphology-dependent effect in electrocatalysis. Fig. 6 shows the oxidation of an adsorbed CO monolayer on the Pt NWs and Pt NPs in 0.1 M HClO₄ solution. While our ultrathin NWs had extended crystalline facets and a small portion of surface LCAs, they displayed a markedly negative-potential shift for the CO stripping as compared with commercial NPs. In fact, the corresponding main peak potentials are 0.73 V and 0.90 V, respectively. That is, the Pt NWs exhibited a significantly higher CO oxidation activity (based on the main stripping peak) than the Pt NPs. A similar observation of enhanced CO oxidation activity on carbon supported Pt NWs as compared with their 0-D counterparts has also been reported [15]. In addition to the negatively shifted peak potential of CO stripping, a small but clearly discernable CO oxidation feature in the so-called pre-ignition potential region, well below the peak



Fig. 6. Voltammetric curves for CO monolayer stripping on Pt nanowires (a) and nanoparticles (b) in 0.1 M HClO₄ solution. Scan rate: 50 mV s^{-1} . Shown are the first scan (solid line) starting at 0.07 V and the second scan (dash-dot line). The electrode was exposed to dissolved CO for 5 min at 0.07 V followed by Ar bubbling for 20 min. Typical HRTEM images of a Pt nanowire (a) and nanoparticle (b) are also shown. The scale bar is 2 nm for both images.

potential (E<0.6 V), was also observed on the Pt NWs but was absent on the Pt NPs. A similar feature for CO oxidation in the pre-ignition potential region has been previously reported on wellordered Pt surfaces with so-called "defect sites", which play a critical role in CO oxidation at low potentials [29,40,41]. The existence of these active sites is a very important indicator for a high CO poisoning resistance catalyst, because CO oxidation at this low potential region can free more surface sites for reactant adsorption and reaction [29,40,41]. Note that the surface coverage of CO_{ads} formed during the EOR begins to decrease at a significantly lower potential on the Pt NWs, in line with the characteristic voltammetric feature of CO oxidation at the pre-ignition potential region. The enhanced activity for CO monolayer oxidation may possibly be a consequence of the unique structural and electronic properties of our ultrathin nanowires.

On the other hand, recent studies have suggested that the agglomeration of Pt nanostructures that generates large amounts of defect sites also increases the CO oxidation activity [3,5,6,42,43]. However, based on a preponderance of previous results, we believe that the enhanced CO stripping arises from an intrinsic difference in the electrocatalytic properties of ultrathin Pt nanowire morphology. Specifically, our CV data and previous ORR work [14] suggested that the Pt NWs possess fewer surface defects when compared with associated 0-D analogues. Furthermore, we did not observe any significant effect of particle dispersion on the ORR activity of these nanowires in our previous ORR study [14], highlighting the intrinsic relationship between the structure of 1-D nanostructure and their electrocatalytic activity, as opposed to agglomeration effects. However, the effects of the aggregation may not be ruled out entirely because of the complexity of this hierarchical nanowire network structure. Regardless, the data presented in Fig. 6 provides evidence for the presence of unique sites that are active toward CO oxidation, which is further justification for the high activity and poisoning resistance in ethanol oxidation observed in the case of the ultrathin Pt nanowires.

It has been previously reported that Pt nanoparticles with a high density of surface LCAs usually generated a correspondingly high activity for the EOR [2,8]. However, our Pt 1-D nanostructure has a morphology that is clearly different from this category. Therefore, the highly enhanced catalytic activity and selectivity in ethanol oxidation and CO monolayer stripping on Pt catalysts with 1-D nanostructures as compared with associated 0-D analogues raises very interesting questions. Herein, we believe that the enhanced catalytic performance of nanowires may be assigned to its unique structural property, that is, a specific ensemble of surface terracedefect sites that are favored in different reaction steps in ethanol oxidation. A series of reactions involving C-dehydrogenation, C-C bond splitting, and -CH_x oxidation that generates the chemisorbed CO intermediate at low potentials in the EOR requires the presence of multiple contiguous sites (terrace sites) [25,29,44]. At potentials where the CO and $-CH_x$ oxidation rate is smaller than the formation rate, the chemisorbed CO and -CH_x accumulate on the surface and act as a catalytically poisoning adsorbate, blocking Pt sites and also affecting nearby sites for further ethanol adsorption and oxidation. Considering the small portion of available terrace sites on 2-3 nm particles, their smaller electrocatalytic activity as compared with nanowires, therefore, could be rationalized due to quickly diminished terrace sites that are required for ethanol adsorption and dehydrogenation. Consistent with this hypothesis of a CO_{ads} and -CH_x inhibiting effect is the onset shift of ethanol oxidation on a surface partially covered with CO_{ads} and –CH_x intermediate (Fig. 2). Therefore, a delicate balance of surface terrace and defect sites on 1-D nanostructures may be conducive to a high ethanol oxidation activity.

Furthermore, the unique structure property of 1-D morphology has also been advantageous in enhancing CO_{ads} diffusion due to their proportionally fewer LCA sites, since CO binds stronger on the LCAs [45-47]. In addition, it has been reported that a significant surface contraction and phase transformation may occur for the thin Pt nanowires when its diameters decreased below 2 nm [14,15,19,21]. Based on Nørskov and Hammer theory [48,49], a down-shift of the *d*-band center due to a surface contracting strain effect will decrease the adsorption strength of reactants. Recently, Wang et al. [15] reported a negative shift of the Pt 4f core-level binding energy, an experimental measure of the relative *d*-band center [48], for carbon supported Pt NWs as compared with NP analogues for the first time. This electronic change was accompanied by a weakening of the interaction with surface adsorbates. Not surprisingly, the unsupported ultrathin Pt nanowires in this report show a corresponding shift in the oxide reduction feature to higher potentials, which suggests a similar structure dependent electronic effect.

In the case of ethanol oxidation, this structure dependent electronic change of the Pt NWs may lead to a weaker binding of CO and thereby improve its surface diffusion rate, which may lead to an enhanced oxidation rate. Heinen et al. [34] have reported that the rate determining step is the removal of surface CO_{ads} poisoning rather than the C-C bond splitting at low potentials for the EOR on the polycrystalline Pt surface. Therefore, it is hypothesized that the high EOR activity on 1-D nanostructures may also possibly be due to their unique structural and electronic properties that lead to efficient removal of surface CO_{ads}. It is critical to highlight, however, that we cannot conclusively comment on the effects of the 1D morphology and structure with respect to the oxidation of adsorbed $-CH_x$ intermediates on the basis of the existing experimental data. Regardless, this interpretation is consistent with results from IRRAS and CO stripping experiments that surface CO_{ads} can be removed at lower potentials on nanowires than on nanoparticles. At high potentials where O/OH adsorption is facile and CO_{ads} coverage is small, a competition between O/OH adsorption and ethanol oxidation will occur on the surface. In a similar manner to the CO poisoning effect, the presence of stabilized O/OH species with large coverage could also impede the EOR. Therefore, the surface that has a weaker OH binding strength can provide for more sites for ethanol oxidation that will lead to high activity. Admittedly, an accurate quantitative evaluation of CO, CO₂, and acetic acid formation is difficult to accomplish by IRRAS measurements alone, due to the thin layer configuration in nanostructured material studies [38]. Therefore, the present interpretation based on IRRAS data is qualitative in nature. Nevertheless, analysis of the CO formation trend and also the ratio between CO₂ and acetic acid production with applied potentials provide for very useful mechanistic insights into this morphology-dependent activity in the EOR.

4. Conclusions

Our work clearly demonstrates the morphology effect on the reaction rates of ethanol oxidation and CO monolayer oxidation on Pt. Namely, the Pt catalyst with 1-D morphology evinces a structure comprised of a specific ensemble of large crystal facets and a small density of defect sites distinctly different from the commercial Pt catalysts with 0-D nanostructures. Electrocatalytic tests have demonstrated that 1-D nanostructures with this structure exhibited greatly enhanced activity and efficiency in the EOR, a negatively shifted onset potential for \sim 0.22V, and a high current density with at least a two-fold enhancement in the potential region of 0.2-0.9V as compared with associated 0-D counterparts. The markedly high activity of CO monolayer oxidation seen also on the 1-D nanostructures, coupled with the observation of chemisorbed CO_{ads} intermediates in the EOR, provides evidence that the unique structural and electronic properties of 1-D nanostructures can lead to an efficient removal of surface CO_{ads}. Therefore, the enhanced

catalytic performance of 1-D nanostructures in the EOR may be attributed to the likely interplay between balanced terrace-step sites for ethanol adsorption and reaction as well as a facilitated removal of chemisorbed CO on the nanowires. These results are clearly different from previous conclusions in which it was advocated that Pt nanostructures with a high density of low coordination atoms are preferred in the EOR [2,8]. Although the detailed mechanism for this morphology-dependent activity still remains elusive, our results evidently show that the morphology of nanostructured catalysts could have a far more profound effect than anticipated in a complex surface reaction such as the ethanol oxidation reaction. These results therefore are of importance in providing needed structural insight into the rational design of and search for novel nanostructured materials in ethanol electrocatalysis.

Acknowledgements

This work was supported in part by U.S. Department of Energy, Divisions of Chemical and Material Sciences, under the Contract No. DE-AC02-98CH10886. Synthesis and characterization work (CK and SSW) on nanowires was supported by the U.S. Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division. WPZ thanks for the financial support from the LDRD program at Brookhaven National Laboratory.

References

- [1] A. Wieckowski, E.R. Savinova, C.G. Vayenas (Eds.), Catalysis and Electrocatalysis at Nanoparticle Surfaces, Marcel Dekker, Inc., New York, 2003.
- [2] N. Tian, Z.-Y. Zhou, S.-G. Sun, Y. Ding, Z.L. Wang, Science 316 (2007) 732.
- [3] M. Arenz, K.J.J. Mayrhofer, V. Stamenkovic, B.B. Blizanac, T. Tomoyuki, P.N. Ross, N.M. Markovic, J. Am. Chem. Soc. 127 (2005) 6819.
- [4] S. Park, Y. Xie, M.J. Weaver, Langmuir 18 (2002) 5792.
- [5] F. Maillard, M. Eikerling, O.V. Cherstiouk, S. Schreier, E. Savinova, U. Stimming, Faraday Discuss. 125 (2004) 357.
- [6] F. Maillard, E.R. Savinova, U. Stimming, J. Electroanal. Chem. 599 (2007) 221.
- [7] J.X. Wang, H. Inada, L. Wu, Y. Zhu, Y. Choi, P. Liu, W.-P. Zhou, R.R. Adzic, J. Am.
- Chem, Soc. 131 (2009) 17298. [8] Z.-Y. Zhou, Z.-Z. Huang, D.-J. Chen, Q. Wang, N. Tian, S.-G. Sun, Angew. Chem. Int. Ed. 49 (2010) 411.
- [9] M. Subhramannia, V.K. Pillai, J. Mater. Chem. 18 (2008) 5858.
- [10] S.W. Lee, S. Chen, W. Sheng, N. Yabuuchi, Y.-T. Kim, T. Mitani, E. Vescovo, Y. Shao-Horn, J. Am. Chem. Soc. 131 (2009) 15669.
- [11] I.Y. Chen, B. Lim, E.P. Lee, Y.N. Xia, Nano Today 4 (2009) 81.
- [12] Y. Takasu, T. Iwazaki, W. Sugimoto, Y. Murakami, Electrochem. Commun. 2 (2000) 671.

- [13] S. Sun, F. Jaouen, J.-P. Dodelet, Adv. Mater. 20 (2008) 3900.
- [14] C. Koenigsmann, W.-P. Zhou, R.R. Adzic, E. Sutter, S.S. Wong, Nano Lett. 10 (2010) 2806.
- S. Wang, S.P. Jiang, X. Wang, J. Guo, Electrochim. Acta 56 (2011) 1563. [15]
- [16] C. Koenigsmann, S.S. Wong, Energy Environ. Sci. 4 (2011) 1161.
- [17] H. Wang, C.W. Xu, F.L. Cheng, S.P. Jiang, Electrochem. Commun. 9 (2007) 1212.
- [18] H. Zhou, W.-P. Zhou, R.R. Adzic, S.S. Wong, J. Phys. Chem. C 113 (2009) 5460.
- [19] M.I. Haftel, K. Gall, Phys. Rev. B 74 (2006) 035420.
- [20] Y. Kondo, K. Takayanagi, Science 289 (2000) 606.
- [21] E. Santos, P. Quaino, G. Soldano, W. Schmickler, Electrochem. Commun. 11 (2009) 1764.
- [22] C. Koenigsmann, A.C. Santulli, K. Gong, M.B. Vukmirovic, W.-P. Zhou, E. Sutter, S.S. Wong, R.R. Adzic, J. Am. Chem. Soc. 133 (2011) 9783.
- [23] M.T.M. Koper, S.C.S. Lai, E. Herrero, in: M.T.M. Koper (Ed.), Fuel Cell Catalysis: A Surface Science Approach, John Wiley & Sons, Inc., Hoboken, New Jersy, 2009.
- [24] D.J. Tarnowski, C. Korzeniewski, J. Phys. Chem. B 101 (1997) 253. [25] F. Colmati, G. Tremiliosi-Filho, E.R. Gonzalez, A. Berna, E. Herrero, J.M. Feliu, Phys. Chem. Chem. Phys. 11 (2009) 9114.
- [26] A.A. Abd-El-Latif, E. Mostafa, S. Huxter, G. Attard, H. Baltruschat, Electrochim. Acta 55 (2010) 7951.
- [27] S.C. Chang, L.W.H. Leung, M.J. Weaver, J. Phys. Chem. 94 (1990) 6013.
- [28] H.A. Gasteiger, N. Markovic, J.P.N. Ross, E.J. Cairns, J. Phys. Chem. 97 (1993) 12020.
- [29] J.S. Spendelow, Q. Xu, J.D. Goodpaster, P.J.A. Kenis, A. Wieckowski, J. Electrochem. Soc. 154 (2007) F238.
- [30] N.P. Lebedeva, M.T.M. Koper, J.M. Feliu, R.A. van Santen, J. Phys. Chem. B 106 (2002) 12938.
- [31] A.V. Tripkovic, K.D. Popovic, J.D. Lovic, V.M. Jovanovic, S.I. Stevanovic, D.V. Tripkovic, A. Kowal, Electrochem. Commun. 11 (2009) 1030.
- [32] W.-P. Zhou, K. Sasaki, D. Su, Y. Zhu, J.X. Wang, R.R. Adzic, J. Phys. Chem. C 114 (2010) 8950.
- [33] M.H. Shao, R.R. Adzic, Electrochim. Acta 50 (2005) 2415.
- [34] M. Heinen, Z. Jusys, R.J. Behm, J. Phys. Chem. C 114 (2010) 9850.
- [35] R.B. Kutz, B. Braunschweig, P. Mukherjee, R.L. Behrens, D.D. Dlott, A. Wieckowski, J. Catal. 278 (2011) 181.
- [36] T. Iwasita, E. Pastor, Electrochim. Acta 39 (1994) 531.
- [37] S.C.S. Lai, S.E.F. Kleyn, V. Rosca, M.T.M. Koper, J. Phys. Chem. C 112 (2008) 19080. [38] M. Li, A. Kowal, K. Sasaki, N. Marinkovic, D. Su, E. Korach, P. Liu, R.R. Adzic,
- Electrochim, Acta 55 (2010) 4331.
- [39] Q. Wang, G.Q. Sun, L.H. Jiang, Q. Xin, S.G. Sun, Y.X. Jiang, S.P. Chen, Z. Jusys, R.J. Behm, Phys. Chem. Chem. Phys. 9 (2007) 2686.
- [40] A. Wieckowski, M. Rubel, C. Gutierrez, J. Electroanal. Chem. 382 (1995) 97.
- [41] N.M. Markovic, J.P.N. Ross, Surf. Sci. Rep. 45 (2002) 117.
- A. López-Cudero, J. Solla-Gullón, E. Herrero, A. Aldaz, J.M. Feliu, J. Electroanal. [42] Chem. 644 (2010) 117. [43] E.G. Ciapina, S.F. Santos, E.R. Gonzalez, J. Electroanal. Chem. 644 (2010) 132.
- S.-C. Chang, Y. Ho, M.J. Weaver, Surf. Sci. 265 (1992) 81. [44]
- [45] B. Hammer, Top. Catal. 37 (2006) 3.
- [46] A.D. Karmazyn, V. Fiorin, S.J. Jenkins, D.A. King, Surf. Sci. 538 (2003) 171.
- [47] B.E. Hayden, K. Kretzschmar, A.M. Bradshaw, R.G. Greenler, Surf. Sci. 149 (1985) 394
- [48] B. Hammer, Y. Morikawa, J.K. Nørskov, Phys. Rev. Lett. 76 (1996) 2141.
- [49] B. Hammer, J.K. Nørskov, Adv. Catal. 45 (2000) 71.