Electroanalysis of Ethanol Oxidation and Reactivity of Platinum-Ruthenium Catalysts Supported onto Nanostructured Titanium Dioxide Matrices

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This study concentrates on the development of catalytic materials capable of enhancing oxidation of ethanol particularly at low potentials, i.e. at conditions resembling operation of anodes in low temperature fuel cells. Indeed, the ethanol oxidation currents measured under voltammetric and chronopotentiometric conditions have been significantly increased following dispersing bimetallic PtRu nanoparticles (~4 nm) catalysts over TiO2 (80% anatase, 20% rutile) nanostructures (~20–30 nm) supported onto multi-walled carbon nanotubes. The improvement in activity is attributed not only to better dispersion of PtRu centers (some increase of active surface area) or improved (carbon-nanotube-assisted) propagation of electrons at the catalytic interface but also to the presence of hydroxyl groups and high mobility of protons at neighboring (to PtRu) TiO2. Further, specific interactions between TiO2 and Pt or Ru metallic components are possible. Importance of addition of TiO2 is also evident from kinetic analysis based on measurements of steady-state currents at different concentrations.

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Ethanol is a renewable low-cost biofuel acting not only during simple combustion but also under electrochemical oxidation (catalytic) conditions thus becoming a reactant of potential importance to the technology of low-temperature direct-alcohol fuel cells. In principle, ethanol has high energy density, 29.7 kJ g−1 (23.3 kJ cm−3), moderate toxicity, and it exists as liquid at room temperature what allows its easier handling, transportation and storage. Although ethanol (C2H5OH) is a model di-carbonic (ethyl) alcohol, its electrooxidation is much more complex when compared to the oxidation mechanism of mono-carbonic (methyl) alcohol. Indeed, methanol (CH3OH) can be readily oxidized to the final product, CO2, through the transfer of six electrons.1 Due to high toxicity of methanol and its capability to undergo crossover through proton-conducting membranes to the cathodic compartments of fuel cells, intense research involving other small organic molecules including ethanol2–10 has been recently pursued.

If electrooxidation of ethanol proceeded ideally to carbon dioxide, the reaction would involve twelve electrons; under such conditions, the fuel cell (with an oxygen cathode) would theoretically produce the open circuit potential of 1.14 V. But complete oxidation of ethanol under electrochemical conditions is a complex reaction because the process would require cleavage of the strong C–C bond in the C2H5OH molecule.11–13 Consequently, the reaction rate is rather slow at ambient conditions, and typically acetaldehyde (two-electron oxidation) or acetic acid (four-electron oxidation) are formed during electrooxidations at common Pt-based (e.g. PtRu or PtSn) catalytic systems.

Despite the unique ability of metallic platinum catalysts to break C–C bond in the ethanol molecule, Pt alloys with Ru or Sn tend to produce higher electrocatalytic currents than platinum itself.14,15 Practical utility of bare Pt is largely limited by blocking (poisoning) the available active Pt sites through strong adsorption of the reaction intermediates including CO-type adsorbates. In a case of bimetallic PtRu catalysts, the surface Ru atoms (situated near Pt ones) are believed form readily Ru oxo species active toward the oxidative removal of CO-type passivating species.16,17 Desorption of CO from Pt may also reflect electronic changes in platinum (existing nearby ruthenium atoms) leading to weakening of Pt–CO bonds.18 Among other important issues is good stability of PtRu (e.g. superior relative to PtSn) nanoparticles during their operation under electrocatalytic conditions.

During electrooxidations of small organic molecules, activity of noble metal nanoparticles can also be increased through dispersing them within or onto certain metal oxide nanostructures.9 Representative examples include studies with use of titanium(IV) oxide, tungsten(VI) oxide, zirconium(IV) oxide, any specific interactions between catalytic sites and the metal oxide matrix as well as the system’s interfacial ion and electron transfer processes would be influenced by the distribution of electronic states within the oxide.30 In aqueous acid media, the oxides are covered by hydroxyl groups facilitating proton mobility and influencing the system’s catalytic activity during electrooxidations.

To address the metal-oxide-induced activation of bimetallic PtRu nanoparticles during electrooxidation of alcohols, we explore here model materials: nanostructured titanium(IV) oxide (80% anatase, 20% rutile) as supports for dispersed PtRu (Pt-to-Ru at the 1:1 ratio) nanoparticles. The choice of TiO2 matrix can be rationalized as follows. The oxide exhibits not only unique optical and electronic properties, but it is robust, chemically stable and can act as highly porous (large surface area) support in catalysis.32,34 The increase of activity of platinum during oxidation of ethanol by dispersing it in TiO2 support was attributed to Pt–TiO2 interactions and changes in electronic properties of platinum.35 Regarding electronic effects, it has been postulated that, in presence of TiO2, the oxygen-containing species (OHads) are formed on Pt at lower potentials (in comparison to bare platinum). These hydroxyl species are believed to induce oxidation of poisoning adsorbates from platinum.36 Because we consider here bimetallic PtRu catalysts, TiO2 should also facilitate formation of hydroxyl groups on ruthenium component and thus enhance Ru activity toward the oxidative removal of CO-like intermediates. TiO2 is well known to co-exist and interact with Ru oxo species within RuO2/TiO2 dimensionally-stable catalytic-anoles.

To improve charge distribution at the semiconducting-titania-containing electrocatalytic interface, the oxide nanostructures have been supported onto the high-surface-area well-conducting carbon carriers.39,40 In this respect, multi-walled carbon nanotubes (CNTs) and graphene nanoribbons seem to be promising. In particular, CNTs are well-appreciated model carbon carriers characterized by good mechanical properties, high electrical conductivity and resistance to corrosion. Typically CNTs are pre-treated to improve their ability to anchor catalytic nanostructures.

In the present work, we have modified CNTs with TiO2 nanostructures and combined them with catalytic PtRu nanoparticles.
Diagnostic experiments have included electrochemical (voltammetric and chronoamperometric) measurements in acid solutions containing ethanol (or methanol for comparison). Special attention has been paid to the systems’ electrocatalytic performance at the relatively low (less positive) potentials (e.g. 0.3–0.4 V) at which oxidations of alcohols are likely to proceed in real low-temperature fuel cells. The results are further discussed and analyzed using the kinetic approach (utilizing results obtained at different concentrations of ethanol) analogous to that commonly used in the enzymatic bioelectrocatalysis.\(^{45-46}\) We demonstrate here that, in the presence of TiO\(_2\) (particularly CNT-supported TiO\(_2\)), the electrocatalytic activity of bimetallic PtRu nanoparticles is enhanced during electrooxidation (in acid medium) of both ethanol and methanol. Our research parallels recent attempts by others\(^{47}\) to utilize TiO\(_2\)-embedded carbon nanofiber supports for PtRu in direct ethanol fuel cells. The observations seem to be of general importance to the development of catalytic materials for electrochemical energy conversion devices.

**Experimental**

As a rule chemical reagents were analytical grade materials. Platinum ruthenium (PtRu) nanoparticles (Pt:Ru 50:50) were purchased from Alfa Aesar. Nanostructured TiO\(_2\) powder (P25) was from Degussa AG. Multiwalled carbon nanotubes (CNTs) and the Nafion polyelectrolyte solution were obtained from Aldrich. Sulfuric acid and ethanol were from POCh (Gliwice, Poland).

All solutions were prepared using doubly-distilled and subsequently deionized (Millipore Milli-Q) water. They were deoxygenated by bubbling with high purity nitrogen. Measurements were made at room temperature (22 ± 2°C).

All electrochemical measurements were performed using a CH Instruments Model 760D workstation (Austin, TX, USA) in three electrodes configuration. The glassy carbon working electrode was utilized in a form of the disk of geometric area, 0.071 cm\(^2\). The reference electrode was the K\(_2\)SO\(_4\)-saturated Hg\(_2\)SO\(_4\) electrode, and the counter (and deposition of traces of metallic Pt at working electrode) than platinum, was used to avoid possible oxidative corrosion of the Pt carbon rod was set as the counter electrode. Here inert carbon, rather than platinum, was used to avoid possible oxidative corrosion of the Pt counter electrode. Here inert carbon, rather than platinum, was used to avoid possible oxidative corrosion of the Pt counter (and deposition of traces of metallic Pt at working electrode) during prolonged voltammetric potential cycling. All potentials were expressed in the present work versus Reversible Hydrogen Electrode (RHE).

Commercial (Degussa) P25 TiO\(_2\) powder, composed of ca. 80% anatase and 20% rutile, was used to deposit titania nanoparticles having ca. 20–30 nm diameters. To achieve this goal, 0.01 g of TiO\(_2\) powder was weighed and subsequently dispersed in 1.25 cm\(^3\) of deionized water using the ultrasonic bath. The suspension of TiO\(_2\) (2 μm\(^3\)) was next deposited onto surface of the glassy carbon disk electrode and, subsequently, dried in air at room temperature (22°C) for 30 min.

Multi-walled carbon nanotubes (CNTs) were prepared by dispersing 50 mg of them using ultrasonic bath in 5 cm\(^3\) of deionized water. To modify glassy carbon electrode with carbon nanotubes, the suspension of CNTs (2 μm\(^3\)) was deposited on the electrode and dried in air. To produce colloidal solution of the titanium oxide (TiO\(_2\))-modified CNTs, 50 mg of nanotubes was dispersed in 5 cm\(^3\) of 20 mmol dm\(^{-3}\) TiO\(_2\) aqueous solution. Then the suspension was sonicated for 2 h. Subsequently, it was centrifuged, and the supernatant suspension was removed and replaced with fresh TiO\(_2\) solution. The centrifuging procedure was typically repeated 3–4 times. Each time TiO\(_2\) solution was decanted. Later, the particles were centrifuged and washed out with water at least 4–5 times to make sure that all free (i.e. not attached to CNTs) species were removed. A drop (2 μm\(^3\)) of this colloidal suspension was introduced onto the glassy carbon surface. Dry samples of CNTs modified with TiO\(_2\) were subjected to elemental analysis (at Center of Chemical and Biological Sciences, University of Warsaw), and the relative mass ratio of TiO\(_2\) to CNTs was estimated to be on the level 40%.

Suspensions (inks) of PtRu nanoparticles were prepared by dispersing 7.1 mg of the PtRu commercial sample through sonication for 120 min in 2.0 cm\(^3\) of distilled water to obtain a homogenous mixture. Later 2 μm\(^3\) of the ink was placed onto the previously described bare of CNT-supported TiO\(_2\) layer and dried in air for 30 min. Care was exercised to keep loading of PtRu nanoparticles on the level 100 μg cm\(^{-2}\) in each catalytic system deposited on glassy carbon electrode. Finally, all catalytic systems were over-coated with ultrathin layers of Nafion polyelectrolyte, namely by introducing 1 μm\(^3\) of the Nafion solution (prepared by introducing the commercial Nafion solution into ethanol at 1 to 10 volume ratio) to stabilize and form protective over-layers.

The catalytic materials were pre-conditioned by potential cycling (in the range from 0.04 to 1.04 V vs. RHE) at 10 mV s\(^{-1}\) for 30 min in the deaerated 0.5 mol dm\(^{-3}\) H\(_2\)SO\(_4\) electrolyte. Before representative voltammetric responses were recorded in the ethanol (0.5 mol dm\(^{-3}\)) containing solutions, the electrodes modified with the respective catalytic materials were first subjected to potential cycling (8 full potential cycles at 10 mV s\(^{-1}\)) in the potential range from 0.04 to 1.04 V (vs. RHE). As a rule, before each representative voltammogram was recorded, the working electrode was kept for 20 s (“quiet time”) at the starting potential.

Transmission electron microscopy (TEM) images were obtained with JEM 1400 (JEOL Co., Japan, 2008) equipped with energy-dispersive full range X-ray microanalysis system (EDS INCA Energy TEM, Oxford Instruments, Great Britain) and high resolution digital camera (CCD MORADA, SiS-Olympus, Germany).

**Results and Discussion**

**Microscopic characterization of TiO\(_2\), CNTs, and CNT-supported TiO\(_2\)** — Figure 1 illustrates transmission electron microscopic (TEM) images of (A) multi-walled carbon nanotubes, CNTs; (B) TiO\(_2\) nanoparticles; and (C) TiO\(_2\) supported onto CNTs. The TEM data of Fig. 1A are consistent with the view that CNTs are in a form of tangled, sometimes glued together and randomly oriented carbon nanostructures having diameters on the level 7–9 nm. Pristine TiO\(_2\) nanoparticles (Fig. 1B) have regular shapes and their sizes are comparable: typically, their diameters are within the range from 20 to 30 nm. The data of Fig. 1C implies the presence of both CNTs and TiO\(_2\) nanostructures. In most cases, the metal oxide nanoparticles seem to be attached directly to carbon nanotubes (i.e. to conductive carriers). Only a few TiO\(_2\) nanoparticles form agglomerates situated
Figure 2. Cyclic voltammetric characteristics of (A) TiO$_2$ nanoparticles immobilized on CNTs, (B) PtRu nanoparticles deposited on CNTs, and (C) and PtRu nanoparticles deposited onto CNT-supported TiO$_2$. Electrolyte: 0.5 mol dm$^{-3}$ H$_2$SO$_4$. Scan rate: 10 mV s$^{-1}$.

Electrochemical identity of catalytic systems.— We also provide here (Fig. 2) background voltammetric responses of (A) CNT-supported TiO$_2$, (B) PtRu dispersed onto CNTs, (C) PtRu dispersed onto CNT-supported TiO$_2$. The result of Fig. 2A is consistent with the lack of electroactivity of TiO$_2$ in the investigated range of potentials. The appearance of some current increases around 0.5–0.6 V (Fig. 2A) seems to reflect the existence of redox processes related to interfacial oxidation of carbon components (here CNTs) to carboxylate or aldehyde type surface species. Similar voltammetric feature was observed before for carbon-supported ZrO$_2$ nanostructures. Apparently surface oxidation processes at carbons are induced in presence of the hydroxyl-group rich metal oxide, such as zirconia or titania, nanostructures in acid media. The existence of fairly large background (rectangular shape) voltammetric currents (Fig. 2A) is consistent with recent reports on the feasibility of use of carbon-supported titania nanostructures as materials for electrochemical capacitors.$^{51}$ The results described in Figs. 2B and 2C reflect typical electrochemical behavior of PtRu nanoparticles (deposited on glassy carbon electrode) recorded in acid medium.$^{28,29}$ Obviously, addition of CNTs as carriers for dispersed PtRu has led to some increase of capacitive-type background currents. It is apparent upon comparison of voltammetric curves of Figs. 2B and 2C that, upon introduction of TiO$_2$, the capacitive contribution is somewhat more pronounced. Nevertheless, the voltammetric currents starting at potentials as low as 0.25 V, that are characteristic primarily of the formation (at PtRu) of ruthenium oxo species and, at more positive potentials, platinum oxides,$^{52}$ seem to be better defined (if not enlarged) in presence of TiO$_2$. Consequently, some attention has been paid to possible changes in the degree of dispersion (increase of the electrochemically active surface area) of PtRu nanoparticles deposited onto CNT-supported TiO$_2$.

Estimation of active surface areas of PtRu (CNT-supported) in presence and absence of TiO$_2$.— It is reasonable to expect that, at the real electrocatalytic interface, smaller PtRu nanoparticles (diameters, ca. 4 nm) would adhere to larger (diameters, ca. 20–30 nm) TiO$_2$ nanostructures thus diminishing possibility of PtRu agglomeration. To comment whether bringing PtRu near or into close association with TiO$_2$ would change significantly the surface active area of PtRu catalytic centers, we have performed additional diagnostic experiments involving underpotential deposition (upd) of copper followed by the voltammetric stripping of Cu metal in manner described earlier.$^{53,54}$ Copper undergoes upd on both platinum and ruthenium readily.

nearby carbon nanotubes. Some of these agglomerates (consisting of 2–5 TiO$_2$ nanoparticles) are in contact with two or more carbon nanotubes. Under such conditions, transfer of charge through CNTs to semiconducting TiO$_2$ nanostructures is feasible. For simplicity, we do not provide TEM images of bimetallic PtRu nanoparticles. These catalytic nanostructures were described earlier,$^{27,29}$ and they are known to have diameters on the level of 4 (±2) nm. Obviously, the degree of dispersion and morphology (and thus the electrochemically active surface area) of PtRu nanoparticles could be affected by the presence and possible interactions with titania nanostructures. This problem will be addressed later in the text.
Electrooxidation of ethanol at hybrid systems.— Figure 4 illustrates cyclic voltammetric responses for electrooxidation of ethanol (dotted lines) at glassy carbon electrode modified with PtRu dispersed onto (A) CNTs and (B) TiO2-supported CNTs. Solid lines (Fig. 4) stand for background voltammetric currents recorded in the ethanol-free 0.5 mol dm$^{-3}$ H$_2$SO$_4$ electrolyte. It is commonly accepted$^{35-57}$ that electrooxidation of ethanol at PtRu catalysts (in acid medium) proceeds during positive potential scans (Fig. 4A) predominantly to acetaldehyde (and to some extent to acetic acid)$^{38,59}$, whereas, during the reverse potential scans, the voltammetric responses should be attributed to oxidation of the adsorbed carbonaceous species (e.g. Pt-OCH$_2$CH$_3$, Pt-CHOH-CH$_3$, (Pt)$_2$ = COH-CH$_3$, Pt- COCH$_3$ and Pt-C≡O)$^{38,60,61}$ in addition to the oxidation of acetaldehyde produced during positive potential scans. In cases of both TiO$_2$-free (Fig. 4A) and TiO$_2$-containing (Fig. 4B) systems, the ethanol oxidation (forward) responses are dominated by a broad peak, or – more precisely – by two overlapping peaks, the first one (appearing as shoulder) at about 0.67 V and the second peak at 0.83 V. It is reasonable to expect that these anodic responses are in accordance with activity of PtRu toward oxidation of ethanol leading to the formation acetaldehyde as the predominant product$^{56,59}$ followed by its further oxidation (at more positive potentials) to acetic acid and presumably, to some extent, to CO$_2$.$^{58}$

To confirm this mechanism, and to exclude possibility of further oxidation of the acetaldehyde intermediate at potentials lower than 0.35 V (later considered here during chronoamperometric experiments), we have performed an additional diagnostic experiment under conditions of Fig. 4C, i.e. using PtRu dispersed onto CNT-supported TiO$_2$, but in 0.5 mol dm$^{-3}$ H$_2$SO$_4$ electrolyte containing 0.5 mol dm$^{-3}$ acetaldehyde, CH$_3$CHO, instead of ethanol (Fig. 4B). It is noteworthy that (during positive potential scanning, Fig. 4C) oxidation of CH$_3$CHO is shifted toward more positive potentials (relative to ethanol, Fig. 4B), and it has produced a broad peak at about 0.85 V (Fig. 4C), i.e. at the potentials comparable to those characteristic of the second step (peak) during oxidation of ethanol (the peak at about 0.83 V in Fig. 4B). This result supports our view about electrooxidation (in the forward scan) of ethanol (via acetaldehyde) to acetic acid at potentials higher than 0.7 V. The fact that the reverse (negative-potential-scan) peak appears in the same potential range during voltammetric experiments in ethanol (Fig. 4B) and acetaldehyde (Fig. 4C) implies similarity of the redox processes occurring in both cases: they stand for oxidation of acetaldehyde or related adsorbates or intermediates existing on the PtRu catalytic surface. The observation that acetaldehyde barely undergoes any oxidation at potentials as low as 0.5 V (Fig. 4C, forward scan) supports our view (based on present and literature$^{56,59}$ results) that oxidation of ethanol (Fig. 4B, forward scan) proceeds solely to acetaldehyde in the low potential range. No oxidation of ethanol to products higher than acetaldehyde (e.g. CO$_2$)$^{56,62}$ are expected below 0.5 V.

An important issue of the data of Figs. 4A and 4B is that the voltammetric responses are largely similar except that currents are ca. 70% higher upon incorporation of nanostructured titania to the electrocatalytic interface. Careful comparison of the voltammetric data mentioned above implies that bringing TiO$_2$ near PtRu leads to additional enhancement of the catalyst activity at higher potentials (probably due to the expected interactions of the Ru component, as Ru-oxo species, with TiO$_2$ nanostructures)$^{32,37,38}$ where oxidation of the acetaldehyde intermediate is feasible.$^{58}$ But it is difficult to explain the overall (>70%) enhancement effect only in terms of the increase (40%) of the electrochemically active surface area of PtRu nanoparticles following dispersion at CNT-supported TiO$_2$ (relative to bare CNTs, as apparent of Cu-stripping experiments of Figs. 3A and 3B). To comment on other possible activating phenomena occurring at the hybrid electrocatalytic interface, we have performed additional diagnostic experiments.

First, we have addressed voltammetric characteristics of the PtRu-based systems (with or without TiO$_2$ or CNTs) at relatively low potentials, namely up to 0.38 V (Fig. 5). As expected, the highest ethanol oxidation currents have been observed for PtRu dispersed onto CNT-supported TiO$_2$ (Fig. 5, Curve a). In comparison to the
Figure 4. Cyclic voltammetric responses recorded in the absence (solid lines) and presence (dashed lines) of 0.5 mol dm$^{-3}$ ethanol at PtRu deposited onto (A) pristine CNTs and (B) CNT-supported TiO$_2$. Fig. 4C describes responses as for Fig. 4B except that the dashed line refers to 0.5 mol dm$^{-3}$ acetaldehyde. Electrolyte: 0.5 mol dm$^{-3}$ H$_2$SO$_4$. Scan rate: 10 mV s$^{-1}$.

lowest response of bare (unsupported) Pt-Ru nanoparticles (Fig. 5, Curve d), all other systems, i.e. TiO$_2$-supported PtRu (Fig. 5, Curve c) and CNT-supported PtRu (Fig. 5, Curve b) exhibit higher currents for the oxidation ethanol in the low potential range. Further diagnostic experiments (oriented on potential application in low-temperature alcohol fuel cells) have been based on monitoring and examining long-term current-time (chronoamperometric) responses (Fig. 6) recorded at two selected low potentials, (A) 0.34 and (B) 0.24 V. Once more, the measured currents for the oxidation of ethanol have been relatively the highest for PtRu dispersed onto CNT-supported TiO$_2$. On the whole, the steady-state chronoamperometric performances of PtRu-based systems (Fig. 6) are in agreement with the voltammetric data (Fig. 5). An important issue of these results is that, regardless the absence of CNT carriers, simple addition of TiO$_2$ (as support) increases activity of PtRu, as demonstrated by more than doubling electrocatalytic currents (compare Curves c and d of Fig. 6). Although the electrocatalytic currents are lower than those recorded for the systems utilizing CNT carriers, the enhancement effect is sound (Fig. 6). In this respect, we refer here to our additional results (for simplicity not shown here) of the independent diagnostic copper-stripping experiments (performed as for Fig. 3) showing no sizeable difference in the electrochemically active surface areas of catalytic PtRu nanoparticles regardless of supporting or not supporting onto TiO$_2$ (16.9 versus 16.1 m$^2$ g$^{-1}$, respectively). Here the enhancement effect reflects most likely the existence of large population of hydroxyl groups and high mobility of protons at the TiO$_2$-containing interface.

Discussion of the above chronamperometric data is based on comparison of current density values (in mA cm$^{-2}$) expressed against geometric surface areas. When the respective current values (measured after 1000 s under conditions of Fig. 6) have been normalized against electrochemical surface areas (determined from Cu-stripping voltammetry, as for Fig. 3), the following specific ethanol oxidation currents have been obtained, respectively, using PtRu catalysts...
Figure 6. Chronoamperometric responses recorded at (A) 0.34 and (B) 0.24 V for the oxidation of ethanol (0.5 mol dm$^{-3}$) using PtRu catalysts dispersed onto (a) CNT-supported TiO$_2$, (b) pristine CNTs, (c) CNT-free TiO$_2$, and (d) bare glassy carbon electrode substrate. Electrolyte: 0.5 mol dm$^{-3}$ H$_2$SO$_4$.

Figure 7A illustrates dependencies of steady-state chronoamperometric currents on concentration in the range from 0.1 to 1.0 mol dm$^{-3}$. Each time, the current value (point) has been determined after 1000 s following application of 0.34 V. The experiments have been done for different catalytic systems utilizing PtRu nanoparticles dispersed at the same loading of 100 $\mu$g cm$^{-2}$ onto (a) CNT-supported TiO$_2$, (b) bare CNTs, (c) pristine TiO$_2$, and (d) on bare glassy carbon electrode substrate (i.e. as unsupported PtRu). For all concentrations considered, the highest electrocatalytic current have been obtained for PtRu deposited on CNT-supported TiO$_2$, and the lowest currents have been found at unsupported PtRu.

Kinetic considerations based on steady-state current measurements.— On the basis of our present results (Figs. 4, 5 and 6) and literature reports, it can be rationalized that, at the potential as low as 0.34 V, electrooxidation of ethanol at PtRu-based catalysts proceeds through simple dehydrogenation to acetaldehyde. In other words, the reaction involves two-electrons, and no other parallel pathways (neither oxidation to acetic acid nor to carbon dioxide) are expected under potentials below 0.35 V. To comment on the dynamics of this reaction, we have performed diagnostic chronoamperometric experiments as for Fig. 6 but at different concentrations of ethanol.

Figure 7A illustrates dependencies of steady-state chronoamperometric currents on concentration in the range from 0.1 to 1.0 mol dm$^{-3}$. Each time, the current value (point) has been determined after 1000 s following application of 0.34 V. The experiments have been done for different catalytic systems utilizing PtRu nanoparticles dispersed at the same loading of 100 $\mu$g cm$^{-2}$ onto (a) CNT-supported TiO$_2$, (b) bare CNTs, (c) pristine TiO$_2$, and (d) on bare glassy carbon electrode substrate (i.e. as unsupported PtRu). For all concentrations considered, the highest electrocatalytic current have been obtained for PtRu deposited on CNT-supported TiO$_2$, and the lowest currents have been found at unsupported PtRu.
For all the systems studied (Fig. 7A), the current responses have been linearly dependent on concentration at least up to 0.6 mol dm$^{-3}$ of ethanol. This result is consistent with the pseudo-first-order kinetic pattern. At concentrations higher than 0.6 mol dm$^{-3}$ of ethanol, deviation from linearity is observed, and the current values tend to level off to eventually reach the constant response (what implies the pseudo-zero-order kinetics with respect to concentration). Such behavior permits application of the Michaelis-Menten-type approach to kinetic analysis (proposed together with the Lineweaver-Burk equation for enzymatic kinetics in bioelectrochemistry), because rates of catalytic reactions (here expressed in terms of steady-state electrocatalytic currents as for Fig. 7A) rise linearly as concentrations increase and then begin to level off and approach maxima at higher concentrations. By analogy to enzymatic electroanalysis, we have considered here plots of the reciprocals of current densities on the reciprocals of concentrations (Fig. 7B) that allowed us extrapolations to the infinitely high concentrations and thus determinations of the maximum electrocatalytic current densities, $j_{\text{max}}$. In bioelectrocatalysis, the $j_{\text{max}}$ values often serve as kinetic parameters. Although their practical meaning is different, comparison of the $j_{\text{max}}$ values could also be useful for catalytic PtRu nanoparticles dispersed onto (a) CNT-supported TiO$_2$, (b) bare CNTs, (c) pristine TiO$_2$, and (d) bare glassy carbon electrode. For the systems studied, the following $j_{\text{max}}$ values have been obtained: (a) 0.39; (b) 0.21; (c) 0.13; and (d) 0.08 mA cm$^{-2}$.

Knowing that, in each case, the loading of PtRu catalyst was the same (100 µg cm$^{-2}$), this sequence is consistent with the systems’ relative electrocatalytic activities. Finally, the $j_{\text{max}}$ parameter can be interpreted in terms of the maximum possible catalytic current that can be achieved at the system studied.

Having in mind the Michaelis-Menten enzymatic analysis, we have also estimated concentrations, $C_{1/2 j_{\text{max}}}$, at which the chronoamperometric currents reach the half values of the maximum extrapolated currents (i.e. $1/2 j_{\text{max}}$). These $C_{1/2 j_{\text{max}}}$ are known in enzymatic catalysis as Michaelis-Menten constants (often expressed as $K_M$). Here the kinetic meaning is as follows: for the most efficient electrocatalytic system, the half value of the highest electrocatalytic current ($1/2 j_{\text{max}}$) can be reached at the relatively the lowest $C_{1/2 j_{\text{max}}}$ value. The situation is opposite in a case of the least efficient electrocatalytic system. For the catalytic materials studied here, the $C_{1/2 j_{\text{max}}}$ values have been found between ca. 0.5 and 0.7 mol dm$^{-3}$ ethanol. Furthermore, the lowest $C_{1/2 j_{\text{max}}}$ value (close to 0.5 mol dm$^{-3}$) has been determined for the most efficient system of PtRu dispersed onto CNT-supported TiO$_2$; and the highest $C_{1/2 j_{\text{max}}}$ value (close to 0.7 mol dm$^{-3}$) has been found for the relatively least efficient bare PtRu nanoparticles. Despite the kinetic importance of the $C_{1/2 j_{\text{max}}}$ Concentration, its knowledge permits defining the optimum experimental conditions under which the measured current is not only high but also lies within the linear range of its dependence on concentration.

Finally, additional information about the dynamics of catalytic reactions can be obtained by referring to fundamentals of electrochemical kinetic analysis and by considering the fact that our electrocatalytic systems yield (after 1000 s) steady-state currents (Fig. 6A), as well as they are kinetically slow enough to be described as totally dependent on interfacial charge transfer rates rather than diffusional mass transport, one can refer to the classic kinetic equation, $j = nFk_AC_e^n$, where $j$ refers to current density (here steady-state chronoamperometric response in A cm$^{-2}$), $n$ is a number electrons involved (here $n = 2$ upon assuming oxidation of ethanol predominantly to acetaldehyde), $F$ is Faraday constant (96500 C mol$^{-1}$), $k_A$ is the rate constant for oxidation in heterogeneous units (cm$^2$ s$^{-1}$), and $C_e$ stands for bulk (solution) concentration of the reactant (here 5 x 10$^{-4}$ mol cm$^{-3}$ ethanol). When using the data of Fig. 7, the following rate constants ($k_A$) can be estimated for the systems studied here: (a) $2 \times 10^{-6}$; (b) $1 \times 10^{-5}$; (c) $6 \times 10^{-7}$; and (d) $3 \times 10^{-6}$ cm$^2$ s$^{-1}$. As expected for such an inert process as oxidation of ethanol, these values are low. Although they have approximate meaning, they permit not only valuable comparisons but they also allow us to comment about dynamics of the electrocatalytic systems with use of commonly-accepted heterogenous rate constants (in cm$^2$ s$^{-1}$) as kinetic parameters for electrode processes. For example, it is apparent upon comparison the above $k_A$’s values that addition of TiO$_2$, regardless the presence or absence of CNTs, results in doubling of respective rate constants (compare pairs of $k_A$’s for cases d and e as well as b and a).

**Mechanistic considerations by probing reactivity of systems toward methanol oxidation.**—To further comment on the influence of titania nanostructures on activity of PtRu nanoparticles during catalytic electrooxidations, we performed diagnostic voltammetric measurements with TiO$_2$-free and TiO$_2$-containing systems using the methanol oxidation process as a simple electrocatalytic probe. Indeed, oxidation of methanol proceeds predominantly to CO$_2$, and the reaction involves formation of CO-type intermediates as poisoning adsorbates on noble metal (e.g. Pt) catalytic sites. The latter processes would be of importance when methanolic residues could be formed following C=C bond breaking in ethanol (e.g., in further reasearch, with use of more advanced multi-component catalysts utilizing the TiO$_2$-supported PtRu nanostructures as well).

Figure 8A illustrates background-subtracted voltammetric responses for electrooxidation of 0.5 mol dm$^{-3}$ methanol (in 0.5 mol dm$^{-3}$ H$_2$SO$_4$) at glassy carbon electrode modified with PtRu dispersed onto CNTs (solid lines) and CNT-supported TiO$_2$ (dashed lines). While the voltammetric curves were qualitatively similar, the currents recorded at the system utilizing TiO$_2$ nanostructures were significantly (ca. 50%) higher. Further, by performing experiments with methanolic adsorbates (rather than with methanol dissolved in the electrolyte), we could comment on the relative surface reactivities of bare and TiO$_2$-containing systems (e.g. toward the CO-type surface reaction intermediates). Here, the respective electrocatalytic electrodes were first conditioned in 0.5 mol dm$^{-3}$ methanol (in 0.5 mol dm$^{-3}$ H$_2$SO$_4$) at 0.24 V for 1000 s. After this step, during which methanol formed the adsorbtate layers (certainly on PtRu catalytic centers and, possibly, on adjacent TiO$_2$ nanostructures as well), the electrodes were transferred to the supporting electrolyte. Fig. 8A (Inset) illustrates background-subtracted voltammetric responses (oxidations of the methanol adsorbates) indicating higher oxidative activity (larger current densities) of the system utilizing CNT-supported TiO$_2$ (dashed lines) rather than bare CNTs (solid lines). Regarding the enhancement effect (which may reflect the increase of the electrochemically active surface area of dispersed PtRu and the presence of large population of active hydroxyl groups in presence of TiO$_2$) it is noteworthy that oxidation of methanol adsorbate proceeds in two steps (dashed line in Inset to Fig. 8A with two partially overlapping voltammetric peaks at the titania-containing system). While the first peak (at about 0.45 V) should be correlated with the oxidation of CO-type adsorbates at PtRu, the second more positive wave appears at potentials higher than 0.6 V, i.e. analogous to those characteristic of the oxidation of methanol in solution (Fig. 8A). Thus it is reasonable to expect that, in the presence of titania, methanol adsorbates exist at the electrocatalytic interface in excess relative to the TiO$_2$-free system. Contrary to PtRu nanoparticles, at which methanol molecules are adsorbed, activated and dissociated to CO-type intermediates, the methanol adsorbates existing on hydrated titania nanostructures seem to behave like solution species. The data of Fig. 8A (Inset) are also consistent with high activity of PtRu deposited onto CNT-supported TiO$_2$ toward methanol oxidation at potentials higher than 0.6 V. Mutual activating interactions between titania and Ru oxo species are well-established and postulated for Ru$_2$/TiO$_2$ dimensionally-stable catalytic-anodes.

Ethanol adsorbates can also be formed at the surfaces of catalytic electrodes (as for Fig. 8A) in a manner analogous to the procedure described above for preparation of the methanolic ones. Inset to Fig. 8B illustrates the background-subtracted voltammetric responses for the ethanol adsorbates deposited on the glassy carbon electrode modified with PtRu dispersed onto CNTs (solid line) and CNT-supported TiO$_2$ (dashed line). Here the system’s voltammetric patterns resemble the solution behavior (oxidation) of ethanol (Figs. 4A and 4B). As expected, the ethanol-adsorbate oxidation-currents have been found higher for the TiO$_2$-containing system (dashed line in Inset}
to Fig. 8B). Additional diagnostic experiments have utilized electrocatalytic electrodes with ethanol adsorbates on surfaces of both bare and TiO$_2$-containing catalytic systems. Here the ethanol adsorbates on catalytic surfaces can be considered as “passivating residues” during oxidation of methanol. Upon transferring them to 0.5 mol dm$^{-3}$ methanol (in 0.5 mol dm$^{-3}$ H$_2$SO$_4$) solution, sizeable differences in the methanol-oxidation voltammetric-current-densities have been observed (Fig. 8B). What is even more important upon comparison of the respective data of Figs. 8A and 8B, is that the relative methanol-oxidation current decrease (caused by the presence of ethanol adsorbate on catalytic surface) is significant (ca. 25%) in a case of TiO$_2$-free system but it is basically not existing at the electrocatalytic interface containing TiO$_2$. The present results indicate that any possible poisoning or passivating effects originating from the adsorption of ethanol and methanol or their oxidation products (intermediates) are likely to be less pronounced on PtRu catalytic sites situated nearby TiO$_2$ nanostructures. Further research is along this line.

**Conclusions**

Dispersing of catalytic PtRu nanoparticles over CNT-supported TiO$_2$ (deposited on glassy carbon electrode substrate) has produced an interface highly active toward oxidation of ethanol. The increase of electrocatalytic currents (under both voltammetric and chronoamperometric conditions) has also been apparent at fairly low poten-}

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**References**

1. V. Rao, C. Cremers, U. Stimming, L. Cao, S. Sun, Y. Sun, G. Sun, and Q. Xin, *J. Electrochem. Soc.*, **154**, B1138 (2007).
2. I. Kim, O. H. Han, S. A. Chae, Y. Paik, S.-H. Kwon, K.-Se. Lee, Y.-E. Sung, and H. Kim, *Angew. Chem. Int. Ed.*, **50**, 2270 (2011).
3. S. C. S. Lai, S. E. F. Kleinj, P. T. Z. Ozturk, V. C. van Rees Vellinga, J. Koning, P. Rodriguez, and M. T. M. Koper, *Catal. Today*, **154**, 92 (2010).
4. C. Lamy, S. Rousseau, E. M. Belgis, C. Coutanceau, and J. M. Leger, *Electrochim. Acta*, **49**, 3901 (2004).
5. J. Lobato, P. Canizares, M. A. Rodrigo, and J. J. Linares, *Fuel Cells*, **9**, 597 (2009).
6. S. Rousseau, C. Coutanceau, C. Lamy, and J. M. Leger, *J. Power Sources*, **158**, 18 (2006).
7. F. Vigier, C. Coutanceau, A. Perrard, E. M. Belgis, and C. Lamy, *J. Appl. Electrochem.*, **34**, 439 (2004).
8. W. J. Zhou, W. Z. Li, S. Q. Song, Z. H. Zhou, L. H. Jiang, G. Q. Sun, X. Qin, K. Pouliantitis, S. Kottou, and P. Tsaiarakas, *J. Power Sources*, **131**, 217 (2004).
9. P. J. Kulesza, I. S. Pieta, I. A. Rutkowska, A. Wadas, D. Marks, K. Klak, L. Stobinski, and J. A. Cox, *Electrochim. Acta*, **110**, 474 (2013).
10. J. Mann, N. Yao, and A. B. Bocarsly, *Langmuir*, **22**, 10432 (2006).
11. J. P. I. de Souza, S. L. Queiroz, K. Bergamasaki, E. R. González, and F. C. Nart, *J. Phys. Chem. B*, **106**, 9825 (2002).
12. S.-C. Chang, L.-W. H. Leung, and M. J. Weaver, *J. Phys. Chem.*, **94**, 6013 (1990).
13. T. Iwatsa, *J. Braz. Chem. Soc.*, **13**, 401 (2002).
14. H. Wang, Z. Jusys, and R. J. Behm, *J. Power Sources*, **154**, 351 (2006).
15. Q. Wang, G. Q. Sun, L. H. Jing, Q. Xin, S. G. Sun, Y. X. Jiang, S. P. Chen, Z. Jusys, and R. J. Behm, *Phys. Chem. Chem. Phys.*, **9**, 2686 (2007).
16. T. Vidakovik, M. Christov, and K. Sundinmacher, *J. Electroanal. Chem.*, **580**, 105 (2005).
