Enhanced Electrokinetics of C–C Bond Splitting during Ethanol Oxidation by using a Pt/Rh/Sn Catalyst with a Partially Oxidized Pt and Rh Core and a SnO2 Shell

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Direct ethanol fuel cells (DEFCs) are a promising technology for generating electricity through the electro-oxidation of liquid ethanol. Its implementation requires the development of anode catalysts capable of producing CO2 and yielding 12-electron transfer through breaking the C–C bond of ethanol. Here, we presented comprehensive studies of the electrokinetics of CO2 generation on Pt/Rh/Sn ternary catalysts. Our studies showed that the triphasic PtRhO–SnO2 catalysts with a partially oxidized Pt and Rh core and a SnO2 shell, validated by X-ray absorption analyses and scanning transmission electron microscopy-electron energy loss spectroscopy line scans, coincided with a 2.5-fold increase in the CO2 generation rate towards ethanol oxidation reaction, compared with the biphasic PtRh–SnO2 catalysts with a metallic PtRh alloy core and commercial Pt. These studies provided insight into the design of a new genre of electrocatalysts with a partially oxidized noble metal.

Energy demands coupled with concerns over environmental pollution have created a great need for clean and efficient power sources. Fuel cells that enable the direct conversion of chemical energy to electricity with over 90% thermodynamic efficiency become viable alternative power devices to internal combustion engines where thermodynamic efficiency is subject to the Carnot cycle limitation (typically < 35%). Ethanol, recognized as a substantial energy source in the green technologies, has many advantages over hydrogen gas as a fuel in fuel cells: ethanol has a lower toxicity, a high boiling point for safer storage in transportation applications, a great availability from fermenting sugar-containing and/or cellulose-containing raw materials, and the established infrastructure for production and distribution. In recent years, direct ethanol fuel cells (DEFCs) have been extensively studied, with peculiar attention to their anode reactions, namely the ethanol oxidation reaction (EOR). Ethanol is the simplest molecule containing C–C, C–H, C–O, and O–H bonds, and the selective cleavage of these bonds determines the reaction pathways and relative selectivity of products. For example, EOR through the C–C bond-breakage pathway leads to the production of CO through a complete oxidation of ethanol with a twelve-electron transfer, whereas cleavage of the C–H, O–H, and/or C–O bonds without the C–C bonds lead to incomplete oxidation with production of acetaldehyde (two-electron transfer) or acetic acid (four-electron transfer).1–4

Biphasic PtRh–SnO2 materials with a PtRh alloy and a segregated SnO2 phase have been considered as the best catalyst for EOR owing to their high reactivity for adsorption, dehydrogenation, and oxidation of ethanol by C–C splitting, as well as plausible chemical stability.5–14 The superiority of Pt and Rh towards C–C splitting has been demonstrated by density functional theory (DFT) calculations, showing that Pt–Rh help cleave the C–H bond of the terminal methyl group (β-carbon dehydrogenation) and form oxometallate intermediates (M-CH2-CH2-O-M).15 Oxophilic Sn, on the other hand, interacts with water strongly to form an oxygenated species on the catalyst surface (OHads), which helps oxidize the reaction intermediates (e.g., CH2 and CO) generated on adjacent Pt or Rh sites.16,17 Attributed to this bifunctional effect, Pt/Rh/Sn ternary catalysts have been generally considered as the most effective materials for the EOR, especially at higher overpotentials. However, fuel cells generally tend to operate at an external potential close to their equilibrium potential. At low overpotentials at the anode, the Pt/Rh/Sn components have a weak dissociative adsorption of water, and the resulting low OHads coverage on the catalyst surface may not be adequate to remove the strongly adsorbed reaction intermediates, especially CO, which poisons the active sites. Therefore, finding an optimal catalytic structure that can effectively dissociate ethanol by C–C splitting at low overpotentials and consequently remove the CO intermediates is of great importance for the implementation of DEFC technology.

In the past decade, studies have shown that the kinetics of CO oxidation reaction on surfaces of Ru, Pt, Pd, Rh, and PtRh increases significantly in conjunction with the formation of a thin oxide film on the surface of the metal or alloy...
It has been found that the active phase for CO oxidation is oxidized rather than metallic. Although these results obtained from solid/gas-phase reactions are expected to be relevant for general heterogeneous catalysis, the reactivity of noble metal oxides towards electrocatalysis, especially EOR, has not been well studied. Particularly, most of the studies on Pt-based EOR catalysts have only been focused on non-noble metal oxides, such as SnO2 and CeO2. However, the role of Pt or Rh oxides on the electrokinetics of EOR, especially the C–C splitting, has not been reported.

In this study, we synthesized two types of carbon supported Pt/Rh–SnO2 core–shell nanoparticles: one was triphasic PtRhOx–SnO2 with a partially oxidized Pt and Rh core (segregated Pt and Rh phases) and a SnO2 shell, and the other was biphasic PtRh–SnO2 with a PtRh alloy core and a SnO2 shell. By using our newly designed four-electrode electrochemical cell equipped with a CO2 microelectrode, we comprehensively studied the electrokinetics of CO2 generation, including the CO2 generation rate and CO2 selectivity, with both types of catalysts. Our studies showed that, for the first time, although the PtRh–SnO2 with a PtRh alloy core was still active, the formation of a partially oxidized Pt and Rh core coincides with a 2.5-fold increase in the CO2 generation rate for EOR.

Carbon-supported PtRhOx–SnO2 nanoparticles with a partially oxidized Pt and Rh core and SnO2 shell were synthesized by a “surfactant-free” polyol process using NaPtCl4·xH2O, K3RhCl6·xH2O, and SnCl2 as precursors in an ethylene glycol solution (see the Supporting Information). PtRh–SnO2 nanoparticles with a PtRh alloy core and a SnO2 shell were synthesized by heating PtRhOx–SnO2 nanoparticles under a reducing atmosphere at an elevated temperature. The molar ratio between Pt and SnO2 was kept as 1:1, while the ratio between Pt and Rh was varied from 2:1 to 4:1. Table S1 (in the Supporting Information) summarizes the results from energy-dispersive X-ray spectroscopy measurements of the resulting catalysts, confirming the atomic ratio of Pt/Rh/Sn as 37:20:43 and 39:12:49.

Figure 1 shows transmission electron microscopy (TEM) images of the as-made and reduced carbon-supported Pt37Rh20Sn43 nanoparticles with average sizes of 2.8 ±0.9 nm and 6.5 ±0.9 nm, respectively. TEM images of the as-made and reduced Pt37Rh20Sn43 nanoparticles are shown in Figure S1 in the Supporting Information. All the diffraction patterns of the as-made and reduced Pt/Rh/Sn samples are shown in Figure S2 in the Supporting Information. The X-ray diffraction (XRD) patterns obtained from solid/gas-phase reactions are expected to be relevant for general heterogeneous catalysis, the reactivity of noble metal oxides towards electrocatalysis, especially EOR, has not been well studied. Particularly, most of the studies on Pt-based EOR catalysts have only been focused on non-noble metal oxides, such as SnO2 and CeO2. However, the role of Pt or Rh oxides on the electrokinetics of EOR, especially the C–C splitting, has not been reported.

Figure 1. TEM images of (a) Pt37Rh20Ox(SnO2)x/C and (b) Pt37Rh20(OxSnO2)x/C. (d) EELS line scan across Pt37Rh20–(SnO2)x particle as indicated by the arrow in (c).
indicating the existence of oxidized phases, although there were still discernable metallic Pt and Rh phases observed in both the as-made samples.

The Fourier transform magnitudes of extended X-ray absorption fine structure (EXAFS) data and theoretical fits for Pt, Sn, and Rh of Pt/Rh/Sn catalysts are shown in Figure S3 and Table S3 in the Supporting Information. The best-fit values of coordination numbers of Pt$_{37}$/Rh$_{20}$/Sn$_{43}$ are summarized in Table 1. For the reduced sample, the obtained first-nearest-neighbor Pt-metal ($N_{Pt-M} = N_{Pt-Pt} + N_{Pt-Rh}$) and Rh-metal ($N_{Rh-M} = N_{Rh-Rh} + N_{Rh-Pt}$) coordination numbers all had reasonably similar values within the uncertainties (6.2 ± 0.5 and 9.3 ± 1.6, respectively). That fact, and the other observation that the Pt–Rh and Rh–Pt contributions were required for both Pt and Rh edge analyses, in addition to the Pt–Pt and Rh–Rh contributions, respectively, demonstrated unambiguously the formation of a Pt–Rh alloy. For the as-made sample, however, Pt and Rh appeared to be the segregated phases without alloy formation, as evident from the fact that only Pt–Pt ($N_{Pt-Pt} = 7.4 ± 1.5$) and Rh–Rh ($N_{Rh-Rh} = 1.7 ± 1.1$) coordination was observed without any Pt–Rh and Rh–Pt coordination. Moreover, discernable Pt–O and Rh–O coordination indicated the existence of oxidized Pt and Rh phases. Strong Pt–Pt and Rh–Rh coordination, weak but discernable Pt–O and Rh–O coordination, and non-detectable Pt–Sn and Rh–Sn coordination corroborated well with the XANES analyses, concluding that the as-made Pt$_{37}$/Rh$_{20}$/Sn$_{43}$ catalysts were comprised of partially oxidized Pt and Rh cores.

Independent evidence towards similar conclusions could be concluded from the bond lengths. Table S3 indicates that Pt and Rh exist mainly in the metallic phase in the reduced Pt$_{37}$/Rh$_{20}$/Sn$_{43}$ sample, compared with as-made one. In the former sample, the Pt–Pt bond length (2.73 ± 0.01 Å) and Rh–Rh bond length (2.68 ± 0.01 Å) are similar to that in pure Pt (2.764 ± 0.003 Å) and Rh (2.685 ± 0.002 Å). In the as-made sample, the Pt–Pt bond length (2.67 ± 0.01 Å) and Rh–Rh bond length (2.80 ± 0.03 Å) are rather different from pure metallic Pt and Rh. In addition, the strong Sn–O coordination from both the as-made and reduced samples suggested the formation of tin oxide clusters, which is confirmed by the results obtained independently from STEM–EELS and XANES. Therefore, we concluded the coexistence of the biphase throughout the reduced Pt$_{37}$/Rh$_{20}$/Sn$_{43}$ catalyst, expressed as Pt$_{37}$Rh$_{20}$–(SnO$_2$)$_{43}$: a homogenous alloy core containing Pt and Rh, and SnO$_2$ clusters segregated on the shell; whereas the as-made sample showed a triphase feature expressed as Pt$_{37}$Rh$_{20}$–O$_x$–(SnO$_2$)$_{43}$: a partially oxidized Pt and Rh core with segregated Pt and Rh phases, and SnO$_2$ clusters on the shell. Similar structural details can also be found in as-made and reduced Pt$_{37}$/Rh$_{20}$/Sn$_{43}$ catalysts (Figure S3, Table S3). Moreover, the degree of oxidation (value of $x$) for both Pt and Rh components in Pt$_{37}$/Rh$_{20}$–O$_x$–(SnO$_2$)$_{43}$ catalysts can be estimated by following equation:

$$x = \frac{N_{Pt-Pt} + N_{Rh-Rh}}{N_{Pt-Pt} + N_{Rh-Rh}} \times (37 + 20) = \frac{1.2 + 2.2}{7.4 + 1.7} \times 57 = 21$$

Therefore, the exact formula of partially oxidized catalysts can be expressed as Pt$_{37}$Rh$_{20}$–(SnO$_2$)$_{43}$.

The electrochemical activities of carbon-supported as-made Pt$_{37}$Rh$_{20}$–O$_x$–(SnO$_2$)$_{43}$, its reduced counterpart Pt$_{37}$Rh$_{20}$–(SnO$_2$)$_{43}$, and commercial Pt/C were tested in a half-cell. Figure S4a (in the Supporting Information) shows the cyclic voltammograms (CVs) for the catalysts measured in 0.5 M H$_2$SO$_4$, from which the hydrogen absorption region was used to calculate the electrochemically active surface area (ECASA; Table S2 in the Supporting Information). Figure 2a shows the CV analyses of various catalysts measured in 0.5 M H$_2$SO$_4$ and 0.5 M ethanol electrolyte at a scan rate of 50 mV s$^{-1}$ in the half-cell. The reduced catalyst exhibited superior current density, normalized by its ECASA. The current densities at 0.35 V obtained from CVs measurement are shown in Figure 2b; these follow the order: Pt$_{37}$Rh$_{20}$–(SnO$_2$)$_{43}$ > Pt$_{37}$Rh$_{20}$–O$_x$–(SnO$_2$)$_{43}$ > Pt. The same order was also observed from chronoamperometry measurements (CAs) as shown in Figures 2c and d. These results indicated that Pt$_{37}$Rh$_{20}$–(SnO$_2$)$_{43}$ with a metallic Pt Rh alloy core increased the overall charge-transfer kinetics of the EOR. The high current density observed for the

![Table 1. EXAFS fitting results of Pt/Rh/Sn.](image)

![Figure 2. Electrochemical performance of carbon-supported Pt$_{37}$Rh$_{20}$–(SnO$_2$)$_{43}$, Pt$_{37}$Rh$_{20}$–(SnO$_2$)$_{43}$, and Pt (ETEK) catalysts from (a, b) CVs and (c, d) CAs measurements.](image)
Pt$_{37}$Rh$_{20}$–(SnO$_2$)$_{43}$ catalysts could be attributed to the bifunctional effect as the Pt/Rh atoms provide active sites for dehydrogenation of ethanol, whereas Sn provides oxygenated species to oxidize the intermediates. Such synergistic interactions make Pt$_{37}$Rh$_{20}$–(SnO$_2$)$_{43}$ a better catalyst with fast kinetics for adsorption and dehydrogenation of ethanol molecule.

To better understand the reaction mechanism, especially CO$_2$ generation by C–C splitting during the EOR, we designed a four-electrode electrochemical cell (see the schematic of the cell in Figure S5 in the Supporting Information), including reference, working, and counter electrodes, and a CO$_2$ microelectrode. CV measurements with a scan rate of 0.5 mV s$^{-1}$ were conducted for the EOR by using the four-electrode cell (Figure S6a in the Supporting Information). In addition, the CO$_2$ partial pressure ($P_{CO_2}$) was measured simultaneously by the CO$_2$ microelectrode (Figure S6b). The total amount of CO$_2$ generation ($N_{CO_2}$) was then calculated, as well as the generation rate of CO$_2$. The current density resulting from the generation of CO$_2$ ($j_{CO_2}$) is expressed as:

$$j_{CO_2} = \frac{dN_{CO_2}}{dt} \times 6 \times F$$  \hspace{1cm} (2)

where $F$ is the Faraday constant, and 6 represents the number of electrons transferred upon forming one CO$_2$ molecule. Finally, the selectivity of CO$_2$ generation versus byproduct generation (e.g., CH$_3$CHO, CH$_3$COOH) is calculated by:

$$\text{CO}_2 \text{ selectivity} = \frac{j_{CO_2}}{j_{\text{total}}}$$  \hspace{1cm} (3)

where $j_{\text{total}}$ is the total current, obtained from CV measurements, which represents the current resulting from the formation of all products.

Many studies have been reported on the CO$_2$ generation in situ by using Fourier transform infrared spectroscopy, differential electrochemical mass spectrometry, or gas chromatography [24, 25] from which the concentrations of CO$_2$ as a function of potential were presented. However, to the best of our knowledge, the electrokinetic details of CO$_2$ formation, such as CO$_2$ generation rate and/or selectivity of CO$_2$ generation have not been reported. Thanks to the high sensitivity (towards CO$_2$ concentration of 0.2 μm) and short data acquisition time (five seconds) of the CO$_2$ microelectrode, in this study we were able to provide comprehensive electrokinetic details of CO$_2$ generation by C–C splitting, which has never been reported before.

Figure 3a shows the partial pressure of CO$_2$ recorded simultaneously during the CV measurements by using CO$_2$ microelectrode. Pt$_{37}$Rh$_{20}$O$_{21}$–(SnO$_2$)$_{43}$ showed 2.2 and 3.3 times higher $P_{CO_2}$ as well as a 2.5 times higher CO$_2$ generation rate than Pt$_{37}$Rh$_{20}$–(SnO$_2$)$_{43}$ and commercial Pt at 0.35 V as shown in Figure 3b. Also, the onset potential of CO$_2$ generation ($j_{CO_2}$) was about 37 and 61 mV lower than that of Pt$_{37}$Rh$_{20}$–(SnO$_2$)$_{43}$ and commercial Pt as shown in Figure 3c. Figure 3d shows that Pt$_{37}$Rh$_{20}$O$_{21}$–(SnO$_2$)$_{43}$ displayed higher CO$_2$ selectivity than Pt$_{37}$Rh$_{20}$–(SnO$_2$)$_{43}$ from 0.2 V to 0.35 V, demonstrating 2.8 times higher CO$_2$ selectivity at 0.35 V. These results showed that CO$_2$ generation by C–C bond splitting of ethanol was enhanced on the triphasic Pt$_{37}$Rh$_{20}$O$_{21}$–(SnO$_2$)$_{43}$ with a partially oxidized Pt and Rh core. Notably, although Pt$_{37}$Rh$_{20}$O$_{21}$–(SnO$_2$)$_{43}$ displayed a superior CO$_2$ generation rate, commercial Pt has the highest CO$_2$ selectivity, largely owing to the lower overall current density ($j_{\text{total}}$).

In addition to the discovery of an unexpected promotional effect of the partially oxidized Pt and Rh core on the CO$_2$ generation, we also found that the chemical composition of Pt and Rh played a role in electrokinetics of CO$_2$ generation. Pt/Rh/Sn materials with different Pt and Rh compositions were synthesized, indexed as Pt$_x$Rh$_y$/Sn$_z$. Our electrochemical data showed similar results: in terms of CO$_2$ generation, Pt$_{37}$/Rh$_{20}$/Sn$_{43}$ underperforms Pt$_{37}$/Rh$_{12}$/Sn$_{49}$ (Figure S6, Figure S7, Table S2 in the Supporting Information), but triphasic Pt$_{37}$Rh$_{20}$O$_{21}$–(SnO$_2$)$_{43}$ with a partially oxidized Pt and Rh core indeed outperformed biphasic Pt$_{37}$Rh$_{37}$/Sn$_{49}$ with a PtRh alloy core. The former suggests a Pt to Rh ratio of nearly 2:1 was the optimal composition for CO$_2$ generation, and the latter confirms that a partially oxidized Pt and Rh core has better CO$_2$ generation kinetics than the PtRh alloy core.

The exact mechanism of the promotional effect of the partially oxidized Pt and Rh core found in Pt$_{37}$Rh$_{20}$O$_{21}$–(SnO$_2$)$_{43}$ on the CO$_2$ generation kinetics by C–C splitting is still under investigation. However, it is clear that the ensemble effect, associated with the particular arrangements of the Pt, Rh, and Sn atoms, leads to a synergistic effect in catalytic activity.
O constituents, plays an important role in the C–C splitting of ethanol. In lieu of ethanol dissociation, co-existing metallic and oxidized Pt and Rh might show a special advantage for C–C splitting. According to DFT calculations conducted on the process of CO + 3O₂ → CO₂, the reaction barrier to CO₂ formation is significantly lower if O atoms from the edge of the surface oxide are involved in the CO oxidation, compared with the reaction only involving chemisorbed O atoms. Thus, co-existence of metallic and oxidized Pt and Rh on the surface, provided by our new genre of electrocatalysts, Pt₃₇Rh₂₀O₂₁–(SnO₂)₄₃, are of major importance for understanding the complete electro-oxidation of ethanol on a fundamental level, and will aid in the design of new electrocatalysts that have a partially oxidized noble metal core for various reactions.

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Enhanced Electrokinetcs of C–C Bond Splitting during Ethanol Oxidation by using a Pt/Rh/Sn Catalyst with a Partially Oxidized Pt and Rh Core and a SnO₂ Shell

A partially oxidized Pt and Rh core with a SnO₂ shell exhibited a much higher CO₂ generation rate and CO₂ selectivity than the PtRh alloyed core with SnO₂ shell towards the electro-oxidation of ethanol.