# *Communications*

## An Efficient Bifunctional Electrocatalyst of Methanol Oxidation

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*Summary: $Me_2Pt^{IV}(OMe)(OH)(bpy)$, immobilized within polypyrrole deposited on an ITO electrode, amplifies the current due to electrocatalytic methanol oxidation by 6-fold over an equivalent Pt metal electrode (at +0.67 V vs Ag/AgCl in 1 M MeOH/1 M $H_2SO_4$−$H_2O$).*

The direct methanol−air fuel cell is a promising electrochemical power source for various applications, including energizing cell phones.[1] Unlike the hydrogen−oxygen fuel cell, the device uses a liquid fuel that is easily transported. It is also readily amenable to miniaturization. Significant work has been undertaken to optimize direct methanol fuel cells.[1] However, the central problem of this device—namely, poor catalysis at the methanol electrode—has not been overcome. The half-reaction that occurs at the methanol electrode is

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \qquad (1)$$

On the most efficient Pt-based heterogeneous catalysts, this reaction is not clean. A tenacious methanolic residue of obscure composition is progressively deposited.[1] This slows the reaction and decreases the current by several orders of magnitude.[1] Attempts to overcome this limitation, by using pulsing techniques to remove the residue in situ, have proven largely unsuccessful.[1] Heterogeneous Pt-based catalysts have another important disadvantage. They are typically highly inefficient per Pt atom present. This is arguably because most Pt atoms reside within the bulk of the catalyst and not at its surface, where they are catalytically active. A large-scale uptake of present fuel cell technology would consequently require an annual production of Pt larger than the total mined to date.[1] For these reasons, Pt replacement technologies or more efficient catalysts are needed.[1] In this work we describe a discrete dimethyl Pt(IV) complex that, when doped into conducting polypyrrole, appears to catalyze methanol oxidation more efficiently than an equivalent Pt metal electrode.

In a recent review of methanol fuel cell technology, McNicol, Rand, and Williams have proposed that heterogeneous catalysts of methanol oxidation "must be bifunctional—that is, they must adsorb [bind] water and methanol in the same potential range and preferably close to the methanol reversible potential."[1] They hypothesize that the difficulties involved with heterogeneous Pt catalysts arise in the differing affinities of the methanol and water reactants for Pt. Once adsorbed, these reactants likely also have different reactivities. At the instant of reaction a local excess of one of the reactants conceivably exists. The undesired polymeric residue is suggested to form on Pt because of this inequivalence.

These proposals are supported by the fact that the very best heterogeneous catalysts of methanol oxidation reported thus far are highly dispersed, binary Pt−Ru alloys.[2,3] Thus, Pt metal becomes significantly more active when it is pretreated by spontaneous adsorption of Ru.[2] The resulting catalyst comprises segregated Pt and Ru microislands, along whose interfaces *synergistic* catalysis is possible. Certain metal phthalocyanines and tetramethylcyclams also enhance catalytic methanol oxidation when adsorbed on Pt, albeit to a lesser extent.[4]

Homogeneous species offer an important prospective alternative to heterogeneous catalysts of methanol oxidation. For example, Cu(II) phenanthroline, a variety of Rh and Ir complexes, and certain N-donor chelate complexes of Ru are known to catalyze methanol oxidation, although this is usually only to formaldehyde or formic acid, with formation of $H_2$.[5] Ni tetrakis(3-methoxy-4-hydroxyphenyl)porphyrin polymers coated onto Pt or glassy carbon and cycled by direct electron transfer are, however, reported to cleanly oxidize methanol directly to $CO_2$.[6] Catalytic effects are also achieved with Ni tetraaza macrocycles,[7] poly-Ni(II) curcumin films,[8] and certain Ru(V) oxo complexes in Nafion.[9]

While the mechanisms of these catalysts are not known, it is not unreasonable to suppose that they may generally bind and activate both water, in the form of $OH^-$, and methanol in close proximity to each other. If this is correct, then molecular species that simultaneously bind and activate a single water and a single

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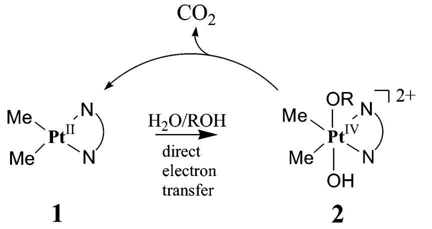
**Scheme 1**



methanol molecule and that undertake a reversible redox cycle should be good candidates for methanol oxidation catalysis. In particular, they potentially eliminate the problem of reactant inequivalence that appears to bedevil heterogeneous catalysts.

Several "bifunctional" species of this type are known. Among these are the dimethyl Pt(II) compounds **1**, first reported by Puddephatt.[10] In the presence of ambient $O_2$, compound **1** undergoes spontaneous and rapid oxidative addition in alcohol−water mixtures, giving **2** (N−N = bpy = 2,2-bipyridyl; R = H, alkyl) (Scheme 1).[10] The methoxy ligand formed by **2** (R = Me) in aqueous methanol is remarkably stable, being inert even to solvolysis.[11]

Given the presence of a single methoxy and a single water ligand in **2** (R = Me) and the likelihood of a redox cycle, we wondered whether **2** (R = Me) could be induced to undertake catalysis of the type shown in Scheme 1, with cycling by direct electron transfer. While several Pt salts catalyze various organic reactions,[12] this possibility has not been examined before, as far as we are aware.

Studies of methanol electrooxidation by heterogeneous catalysts typically employ highly acidic aqueous electrolytes, such as 1 M MeOH/1 M $H_2SO_4$−$H_2O$.[1] Initial studies, therefore, examined the stability of **1** and **2** in such solutions.[13] Compound **1** could be briefly dissolved as a 10 mM solution in 1 M MeOH/1 M $H_2SO_4$−$H_2O$; however, it rapidly commenced to precipitate as **2** (R = Me). Thus, **1** and **2** appear to be kinetically stable in the electrolytes employed, albeit sparingly soluble.

Because of the poor solubility of **1** and **2** (R = Me) in $H_2O$−MeOH mixtures, another method was needed to examine their electrochemical and catalytic properties.

A glassy-carbon electrode was consequently spin-coated with a thin layer of Nafion.[13] This was then doped with **2** (R = Me) by ion exchange in acetonitrile.[13] The resulting Nafion−**2** coating displays the distinctive yellow color of **2**. This color persists, unchanged, when the coating is dipped into a 1 M $H_2SO_4$−$H_2O$ solution. Neutral **1** could not be efficiently doped into a Nafion coating using this approach.

The electrochemical properties of **2** in the Nafion−**2** coating were studied by cyclic voltammetry under an $N_2$ atmosphere. As can be seen in Figure 1a, the uncoated glassy-carbon electrode displays no noticeable oxidation peak in sweeping from −0.2 to +1.0 V. The same is true when the electrode is coated with a thin layer of Nafion according to the preparative procedure employed.[13] When the electrode is coated with Nafion−**2**, however, an oxidation peak is observed to commence at ca. 0.67 V (line A in Figure 1b). The peak maximum occurs at 0.78 V (line I). When methanol is then added in increasing proportions to the electrolyte solution, the commencement of the peak is seen to shift anodically to progressively less positive potentials. However, the peak maximum does not move. Thus, when 1 M MeOH is present in the electrolyte, the peak commences at ca. 0.35 V (line B in Figure 1c); its maximum remains at 0.78 V (line II). The resulting bulge in the current profile between 0.45 and 0.67 V in Figure 1c is typical of methanol oxidation catalysis, being seen also in other systems.[2,14]

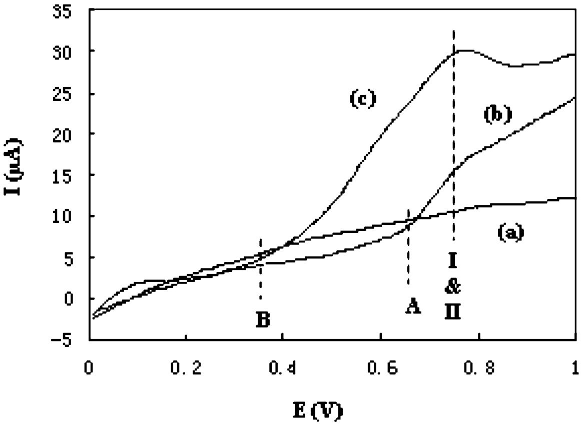


**Figure 1.** Linear voltammograms under $N_2$ vs Ag/AgCl in 1 M $H_2SO_4$/$H_2O$ at a glassy-carbon electrode: (a) uncoated; (b) coated with Nafion−**2** (R = Me); (c) coated with Nafion−**2** (R = Me) with 1 M MeOH in the electrolyte solution. Lines A (+0.67 V) and B (+0.35 V) indicate the onset of oxidation in parts b and c when scanning from left to right. Lines I and II indicate peak maxima.

These results therefore suggest that **2** (R = Me) acts as a methanol oxidation catalyst in, at least, the region 0.35−0.67 V. Given the $N_2$ atmosphere employed, the oxidation process presumably involves direct electron transfer to the electrode.

In order to establish the existence of a catalytic effect, potentiostatic studies were needed. The glassy carbon/Nafion−**2** system is not ideal in this respect, because **2** (R = Me) is progressively leached from the coating when methanol is present in the electrolyte solution.

Compound **2** (R = Me) could, however, be securely immobilized and electrochemically cycled within a polypyrrole (PPy) film grown using so-called vapor-phase polymerization (VPP).[15,16] During VPP, polypyrrole is deposited as a swollen and porous layer on the electrode. When this layer is subsequently washed with acetonitrile, it undergoes dramatic shrinkage, becoming exceedingly dense.[15,16] If a 0.01 M acetonitrile solution of **2** (R = Me) is used in the washing, **2** becomes securely trapped within the polymer. The resulting polypyrrole coating displays a distinctive UV absorption peak at 310 nm due to the **2** (R = Me) in the polypyrrole. This peak persists, unchanged, in VPP-grown polypyrrole (PPy−**2**) deposited on

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(10) Monaghan, P. K.; Puddephatt, R. J. *Inorg. Chim. Acta* **1982**, *65*, L59. Monaghan, P. K.; Puddephatt, R. J. *Organometallics* **1984**, *3*, 444. See also: Rostovtsev, V. V.; Labinger, J. A.; Bercaw, J. E.; Lasseter, T. L.; Goldberg, K. I. *Organometallics* **1998**, *17*, 4530.

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(12) See, e.g.: Rostovtsev, V. V.; Henling, L. M.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **2002**, *41*, 3608 and references therein.

(13) Compounds **1** and **2** were synthesized as described elsewhere.[10] Nafion was employed as a 10% solution in ethanol (Sigma-Aldrich). Nafion films were spin-coated onto glassy-carbon electrodes as follows: 1 $\mu$L of a 10% Nafion solution in ethanol was dropped onto the center of a glassy-carbon-disk electrode (diameter 3 mm) while spinning at a rate of 2000 rpm. The spinning was stopped, and the evenly coated Nafion film was left to air dry for 20 min. The Nafion coating was doped with **2** as follows: once the Nafion coating was dry, it was dipped for 15 min into a 0.5 mM solution of **2** in acetonitrile, with the electrode just below the surface of the solution.

(14) Liu, Y.; Chen, J.; Misoska, V.; Swiegers, G.; Wallace, G. G. *Mater. Lett.*, in press.

(15) Winther-Jensen, B.; Chen, K.; West, K.; Wallace, G. G. *Macromolecules* **2004**, *37*, 5930.

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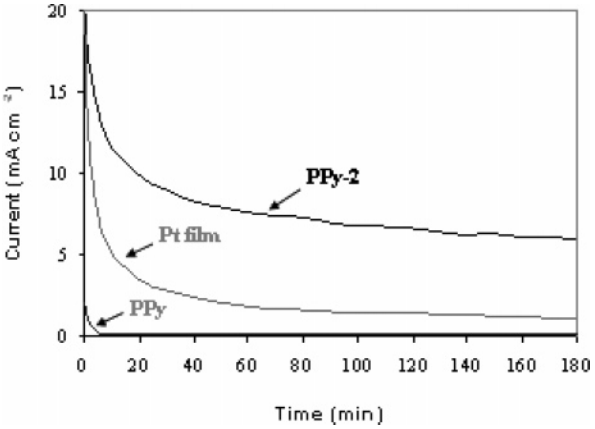

**Figure 2.** Current density (under $N_2$) at +0.67 V (vs Ag/AgCl) for ITO coated with (a) PPy−**2**, (b) PPy, and (c) Pt film, in 1 M MeOH/1 M $H_2SO_4$−$H_2O$.

an indium tin oxide (ITO) electrode,[15,17] even after extended immersion in methanol. The peak is not present in VPP-grown polypyrrole containing only 2,2′-bipyridine.[17]

In order to test the catalytic properties of **2** (R = Me) under potentiostatic conditions, the aforementioned ITO/PPy−**2** electrode was poised for 3 h at +0.67 V (vs Ag/AgCl) in 1 M MeOH/1 M $H_2SO_4$−$H_2O$ under an $N_2$ atmosphere. Figure 2a depicts a representative set of the resulting data. After an initial decline, the current at PPy−**2** levels off, generating a current density of 6.2 mA $cm^{-2}$ after 3 h. A current of this size and persistence can only be due to a sustained catalytic process. This was confirmed by control experiments, in which PPy without any **2** was deposited on ITO electrodes of identical size. When poised at +0.67 V (Figure 2b), these electrodes produced a small initial current due to electrochemical oxidation of the polypyrrole. This process was, however, complete within ca. 10 min. After 3 h, a current density of only 0.08 mA $cm^{-2}$ was obtained.

The catalytic activity of PPy−**2** was compared with that of an identically sized ITO electrode that had been entirely covered by sputter coating with Pt. The resulting Pt-film electrode generated a current density of 1.1 mA $cm^{-2}$ after 3 h of methanol oxidation at +0.67 V. Thus, the PPy−**2**-coated electrode displayed a 6-fold greater rate under near-steady-state conditions. It appears, therefore, that **2** (R = Me) (or an intermediate it generates) is an efficient catalyst of methanol oxidation.

The activity of **2** (R = Me) is consistent with the hypothesized need for a bifunctional capacity in catalysts of methanol electrooxidation. This is likely a requirement of homogeneous, as well as heterogeneous, catalysis. It also seems to be a criterion for the rational design of such catalysts; a capacity for bifunctional binding during redox cycling provides a potential means of identifying candidate catalysts.

Future studies will examine the mechanism of catalysis by **2** (R = Me), as well as its practical utility when immobilized in high densities at the anode surface in a direct methanol fuel cell.

**Supporting Information Available:** Text giving a detailed description of the method employed for vapor-phase polymerization of PPy−**2**, along with figures giving UV−visible absorption spectra of the polypyrrole layer with and without **2** (R = Me) and also of this layer containing only 2,2′-bipyridyl. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) See the Supporting Information.