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VIP Organometallic Fuel Cells

A Biologically Inspired Organometallic Fuel Cell (OMFC) That Converts Renewable Alcohols into Energy and Chemicals**

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The simultaneous conversion of alcohols and sugars into energy and chemicals is a target of primary importance in sustainable chemistry. The realization of such a process provides renewable energy with no CO_2 emission and, at the same time, leads to the production of industrially relevant feedstocks, such as aldehydes, ketones, and carboxylic acids, from biomasses. Two established types of fuel cells operating in alkaline media can convert the free energy of alcohols (RCH_2OH) into electrical energy and the corresponding carboxylate product: the direct alcohol fuel cell (DAFC),[1–6] and the enzymatic biofuel cell (EBFC).[7,8] In a DAFC, an alcohol such as ethanol (CH_3CH_2OH) is selectively converted into acetate (CH_3COO^-) and the electrolyte is an anion-exchange membrane. On the anode, ethanol is oxidized, releasing four electrons [Eq. (1)] that are utilized to reduce one oxygen molecule to four hydroxide ions on the cathode [Eq. (2)]. Efficient devices of this type have been recently developed for a variety of renewable alcohols and polyalcohols, such as ethylene glycol, glycerol, 1,2-propandiol, and C_6 and C_5 sugars.[3–6] (For drawings of a DAFC, a EBFC, and typical power density curves, see the Supporting Information, Figure S1 a–d).

$$\begin{aligned}\text{Anode}\quad & C_2H_5OH + 5\,OH^- \rightarrow \\ & CH_3COO^- + 4\,H_2O + 4\,e^- \qquad E^0 = -0.72\ \text{V}\end{aligned} \tag{1}$$

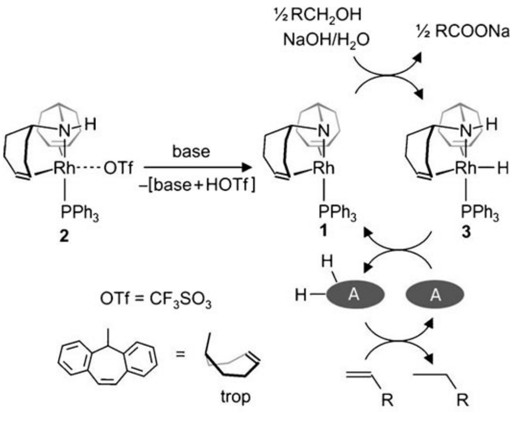
$$\text{Cathode}\quad O_2 + 2\,H_2O + 4\,e^- \rightarrow 4\,OH^- \qquad E^0 = +0.40\ \text{V} \tag{2}$$

$$\begin{aligned}\text{Overall}: \; & C_2H_5OH + O_2 + OH^- \rightarrow \\ & CH_3COO^- + 2\,H_2O \qquad E^0 = +1.12\ \text{V}\end{aligned} \tag{3}$$

In an EBFC, the oxidation of ethanol to acetate involves oxidation enzymes, such as alcohol and aldehyde dehydrogenase, in conjunction with a H^+/electron transfer (Supporting Information, Figure S1 c).[7,8]

We describe another type of fuel cell, named organometallic fuel cell (OMFC), operating in alkaline media where the anode catalyst is a molecular metal complex. We show that in this device, a metal complex evolves through fast chemical equilibria to form specific catalysts for alcohol dehydrogenation, aldehyde dehydrogenation, and H^+/electron transfer.

We recently reported that the organometallic complex $[Rh(trop_2N)(PPh_3)]$ (**1**) catalyses the oxidation of primary alcohols to give carboxylic acid derivatives in the presence of hydrogen acceptors **A** such as RR′C=O, olefins, or palladium nanoparticles in either homogeneous[9,10] or heterogeneous phase (Scheme 1).[11] The amido complex **1** is simply accessed by deprotonation of the precursor complex $[Rh(OTf)(trop_2NH)(PPh_3)]$ (**2**) under basic conditions (OTf = trifluoromethanesulfonate).



Scheme 1. Acceptor-assisted catalytic oxidation of primary alcohols with water to give carboxylates.

We now find that $[Rh(OTf)(trop_2NH)(PPh_3)]$ (**2**) can be deposited intact onto Vulcan XC-72, a conductive carbon support that is often utilized for the preparation of electrocatalysts for DAFCs.[1–3,12]

Inks for the fabrication of electrodes suitable for either cyclic voltammetry (CV) studies or membrane electrode

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assembly (MEA) manufacturing were prepared by standard procedures.[12] The CV response of **2**@C in a 2 M KOH solution did not show any electrochemical activity up to the oxygen discharge potential (Figure 1 a, □). In contrast, a relatively high current density was observed at +0.65 V (vs. the reversible hydrogen electrode (RHE)) by adding a mixture of ethanol/2 M KOH. Such a low onset oxidation potential is typical of the most efficient nanosized palladium electrocatalysts for ethanol oxidation in alkaline media.[1–3,13]

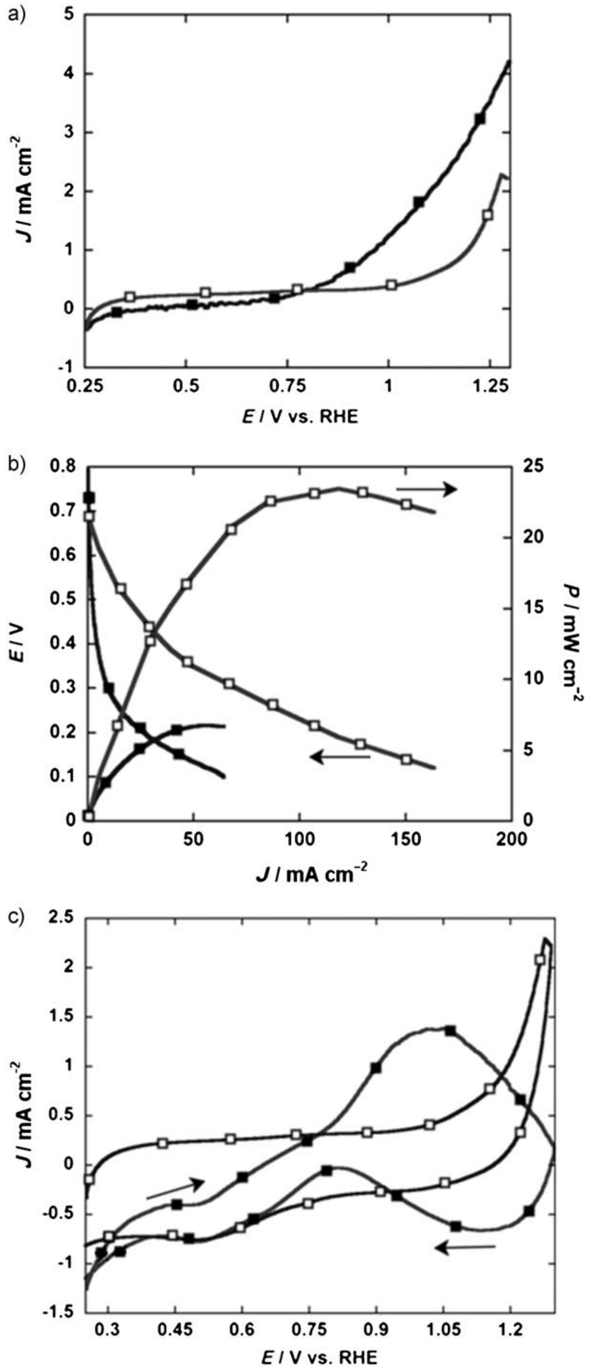
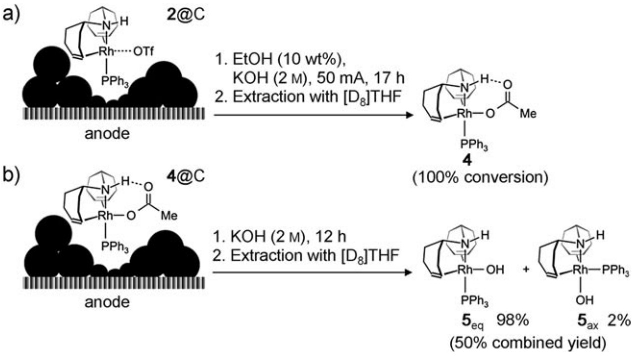


Figure 1. a) CV responses of a glassy carbon electrode coated with **2**@C in 2 M KOH (□) and in 2 M KOH and ethanol (10 wt%) (■). b) Polarization and power density curves of OMFCs fueled with 10 wt% ethanol in 2 M KOH (anode: **2**@C on Ni mesh; cathode: Fe-Co/C on carbon paper; membrane: Tokuyama A006). Air-breathing OMFC at 22 °C (■); active OMFC at 60 °C (□; fuel flow: 4 mL min^{-1}; oxygen flow 0.2 L min^{-1}). c) CV responses of a glassy carbon electrode coated with **3**@C (■) and **2**@C (□) in 2 M KOH.

A MEA was fabricated for a fuel cell comprising a nickel foam anode coated with **2**@C (ca. 1 mg cm^{2} rhodium), a carbon-paper cathode coated with either commercial or proprietary Fe-Co/C electrocatalyst and a Tokuyama A006 anion-exchange membrane.[3–5] The anode compartment was loaded with 10.5 mL of a water solution of ethanol (10 wt %) and 2 M KOH. Figure 1 b shows the polarization and power density curves of this passive cell recorded at 22 °C (■). A maximum power density of 7 mW cm^{-2} was supplied at 22 °C, which is far higher than that of any biofuel cell, yet slightly lower than that observed with a traditional DAFC equipped with a palladium-based anode.[4,13] The power density supplied by the OMFC increases remarkably by increasing the working temperature of the MEA in an active cell under control of the oxygen and fuel fluxes. Indeed, 24 mW cm^{-2} were obtained at 60 °C with a fuel flow of 4 mL min^{-1} and an oxygen flow 0.2 L min^{-1} (Figure 1 b, □).[14] Such a value is still lower than that obtainable with the best anode palladium-based electrocatalysts reported to date (Pd-(Ni-Zn)/C),[4] yet it falls in the upper range of power densities produced by the vast majority of DAFCs containing nanosized noble metal electrocatalysts.[1–3]

The passive OMFC was subjected to galvanostatic experiments at constant currents of 25 and 50 mA. At lower current intensities, the cell kept on working for 44.3 h, producing selectively 14.4 mmol of potassium acetate, which corresponds to 48 % conversion of the starting ethanol. A comparable conversion and selectivity was obtained from the galvanostatic experiment at 50 mA (Supporting Information, Figure S4). Extraction of the used anode by THF gave quantitatively the η^{1}-*O*-acetato complex [Rh(O$_2$CCH$_3$)-(trop$_2$NH)(PPh$_3$)] (**4**; Scheme 2 a). XRPD spectra taken on the electrode after the galvanostatic experiments and on a pure sample of **4** proved that the complex embedded into Vulcan XC-72 is **4**@C. Furthermore, the structural formulation of **4** was confirmed by the independent preparation of this complex and its characterization in both solution (NMR spectroscopy) and solid state.[12] Importantly, ICP-AES anal-



Scheme 2. a) Conversion of complex **2**@C into the acetato complex **4**@C on the electrode surface during the galvanostatic experiment at 50 mA. b) Slow conversion of **4**@C into the catalytically active hydroxo complex **5**@C.

ysis of the anode exhausts after the galvanostatic experiments ruled out any rhodium leaching from the electrode into the solution.

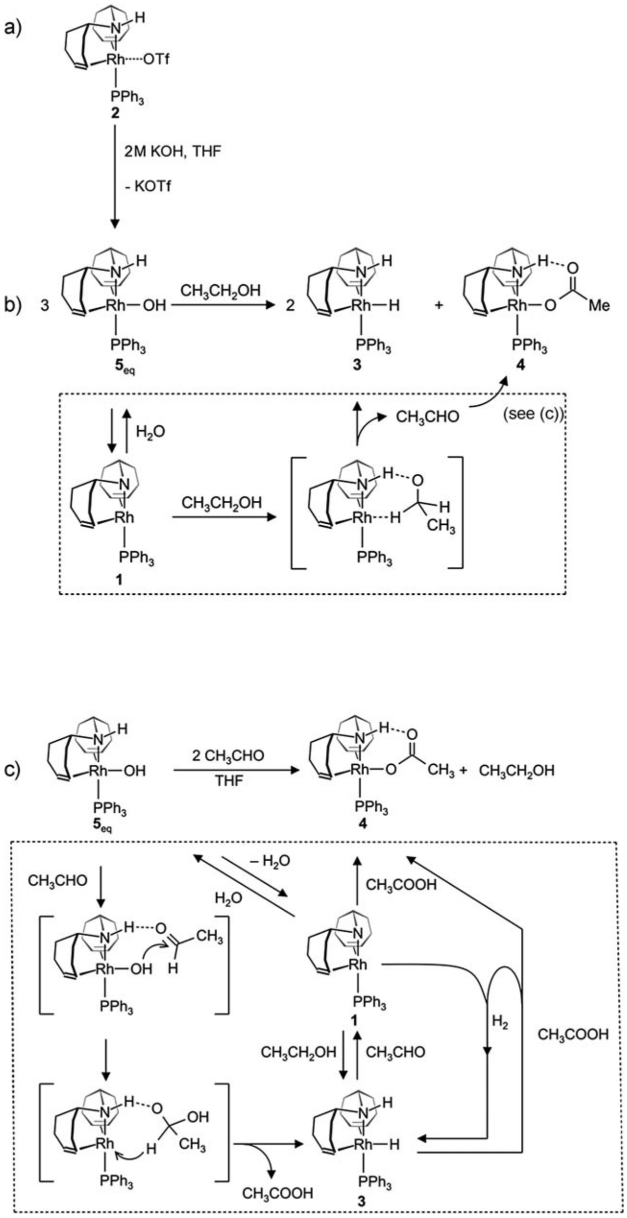
The stability of the acetato complex **4** embedded into Vulcan XC-72 (**4**@C) was investigated (Scheme 2b). When **4**@C was treated with a 2 M aqueous solution of KOH for 12 h and the products subsequently extracted with $[D_8]$THF, 50 % of the acetato complex was still recovered. The other half consisted of the equatorial hydroxo complex $\mathbf{5}_{eq}$, which has a key function in the catalysis along with minor quantities of its axial isomer $\mathbf{5}_{ax}$. We assume that the slow conversion of **4**@C into $\mathbf{5}_{eq}$@C is responsible for the drop of the activity of the cell after about 50 % conversion of ethanol into acetate.

Under open-circuit conditions, **2**@C reacts with the fuel solution at room temperature with no need of external exchange of electrons and after 44 h gives the acetato complex **4** (48.5 %) and the hydride **3** (48.5 %) as major products beside small amounts of the equatorial and axial hydroxo rhodium complexes $\mathbf{5}_{eq}$ (1 %) and $\mathbf{5}_{ax}$ (2 %).

Model reactions in homogeneous solution were performed to rationalize the single reaction steps at the anode surface (Scheme 3). The precursor $[Rh(OTf)(trop_2NH)(PPh_3)]$ **2** reacted immediately with aqueous 2 M KOH to give the equatorial hydroxo complex $[Rh(OH)(trop_2NH)(PPh_3)]$ $\mathbf{5}_{eq}$, which was isolated in more than 95 % pure form after rapid work-up of the reaction mixture (Scheme 3a). Longer reaction times led to conversion of $\mathbf{5}_{eq}$ into the axial isomer $\mathbf{5}_{ax.}$[12] This hydroxo complex $\mathbf{5}_{eq}$ is in rapid equilibrium with the amide complex **1** (Scheme 3b), which is a rare case where a water molecule is added reversibly across a late transition amide bond[15] (an equilibrium constant of $K^{213} = 5\ \mathrm{L\,mol^{-1}}$ was estimated in THF at a temperature of 213 K).

When $\mathbf{5}_{eq}$ was reacted with ethanol in a 3:1 ratio, $[Rh(H)(trop_2NH)(PPh_3)]$ **3** and the acetato complex $[Rh(O_2CCH_3)(trop_2NH)(PPh_3)]$ **4** were obtained immediately in a 2:1 ratio (Scheme 3b). This result is in accord with the reaction mechanism indicated in the dashed box of Scheme 3b.[10] The amide complex **1** is constantly present through the fast equilibrium $\mathbf{5}_{eq} \rightleftarrows \mathbf{1} + H_2O$, and dehydrogenates ethanol in a fast reaction.[16] Acetaldehyde was never detected at any stage of the reaction because it reacts rapidly and selectively with the hydroxo complex $\mathbf{5}_{eq}$ to give the acetato complex **4** and ethanol (Scheme 3c). In the dashed box of Scheme 3c, we show the relevant reactions which rationalize this catalyzed Cannizaro-type disproportion reaction: $2\,CH_3CHO \rightarrow CH_3COOH + CH_3CH_2OH$.[12] 1) The oxidation of acetaldehyde to acetic acid is performed exclusively by the equatorial hydroxo complex $\mathbf{5}_{equiv}$; the axial isomer $\mathbf{5}_{ax}$ is not reactive; 2) The hydride **3** reacts with acetic acid to give the acetato complex **4** and H_2, which in turn is rapidly cleaved across the Rh–N bond of amide **1** to give the hydride **3**;[17] 3) Alternatively, the amide complex **1**, which is present in the reaction mixture by the equilibria $\mathbf{5}_{eq} \rightleftarrows \mathbf{1} + H_2O$ and $\mathbf{3} + CH_3CHO \rightleftarrows \mathbf{1} + CH_3CH_2OH$, adds acetic acid across the Rh–N bond to give **4**. 4) Finally, $[Rh(OH)(trop_2NH)(PPh_3)]$ $\mathbf{5}_{eq}$ reacts with CH_3COOH to give $[Rh(O_2CCH_3)(trop_2NH)(PPh_3)]$ (**4**) and H_2O (not shown in Scheme 3).

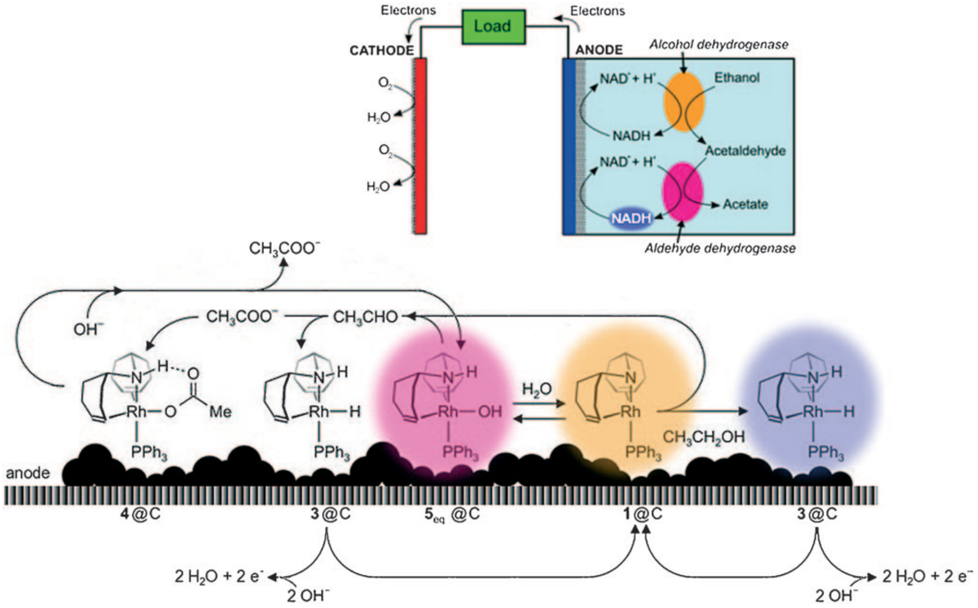
In an experiment where equimolar quantities of propionaldehyde and ethanol were reacted with the hydroxo complex $\mathbf{5}_{eq,}$[12] the propionato complex $[Rh(O_2CC_2H_5)(trop_2NH)(PPh_3)]$ (**6**) was obtained exclusively together with 1-propanol. This clearly shows that a) the hydroxo complex $\mathbf{5}_{eq}$ reacts selectively with aldehydes; b) this reaction is faster than the dehydration of $\mathbf{5}_{eq}$ to the amide **1**; and c) the conversion of aldehyde into carboxylic acid is faster than the dehydrogenation of an alcohol to the corresponding aldehyde.



Scheme 3. Model reactions in homogeneous solution of the precursor complex **2**, the amide complex **1**, and the hydroxo complexes $\mathbf{5}_{eq}$ with KOH, water, ethanol, and acetaldehyde in THF.

Among the several rhodium complexes that are involved in the oxidation of ethanol to acetate, only the hydride $[Rh(H)(trop_2NH)(PPh_3)]$ **3** acts as H-transfer mediator and is ultimately responsible for the current from the OMFC. In this process, **3** is converted into the amide $[Rh(trop_2N)(PPh_3)]$ (**1**), and two electrons are released over the anode with concomitant release of two protons, H^+. Figure 1 c shows the CV response of a glassy carbon electrode coated with **3**@C in 2 M KOH (■) and, by comparison, the response of a similar electrode coated with **2**@C (□). No current was generated by the latter electrode until the oxygen discharge potential was attained, whereas a relatively high current density was generated upon oxidation of **3**@C at the same onset potential observed for **2**@C in a 2 M KOH solution containing 10 wt % ethanol.

The experimental data are in agreement with the mechanism shown in Scheme 4. On the electrode surface, the precursor **2**@C is rapidly converted into the hydroxo complex $\mathbf{5}_{eq}$@C, which is in a rapid equilibrium with the amide **1**@C and water. The amide $[Rh(trop_2N)(PPh_3)]$ dehydrogenates ethanol to acetaldehyde; the aldehyde reacts further with OH^- to form the acetate ion and the hydride **3**@C. The latter complex is oxidized at the electrode releasing two H^+ (neutralized to give water under the basic conditions) and two electrons with regeneration of the amide **1**@C. The stability of the acetato complex **4**@C is responsible for the drop of the current density. At about 50 % conversion, the displacement of the acetate by OH^- to regenerate $\mathbf{5}_{eq}$ becomes too slow and current flow stops.



Scheme 4. Proposed mechanism for the reactions occurring on the surface of the OMFC anode coated with 2@C. The function of an enzymatic biofuel cell (EBFC; top) is included for comparison. Similar colors relate to similar functions (pink: aldehyde dehydrogenation, orange: alcohol dehydrogenation, violet: hydrogen/electron transfer).

There is some resemblance with the enzymatic biofuel cell, but the main characteristic of this system is that one molecular rhodium complex is capable of evolving through fast chemical equilibria in the course of the catalytic cycle to form a specific catalyst for alcohol dehydrogenation (the amide **1**), a specific catalyst for aldehyde dehydrogenation (the hydroxo complex $\mathbf{5}_{eq}$), and a specific catalyst for the H^+/electron transfer (the hydride **3**). In preliminary experiments, we tested other renewable alcohols, and the results obtained with glycerol, ethylene glycol, 1,2-propandiol, and glucose are very encouraging.

It is assumed that nanosized metal electrocatalysts, which are generally platinum-group metals, oxidize alcohols to carboxylic acids via aldehyde intermediates that undergo C–H bond cleavage to form an adsorbed acyl.[1–3,18,19] The coupling of the latter group with adsorbed OH^- gives the carboxylic acid. Herein we propose an alternative mechanism in which no $acyl_{ads}$ is formed and the alcohol dehydrogenation to aldehyde and the aldehyde oxidation to carboxylic acid are carried out by metal–hydroxo species with no need of preliminary C–H bond cleavage (see dashed boxes in Scheme 3 b,c).

The use of a molecular complex as anode electrocatalyst in a DAFC may be a breakthrough in fuel-cell technology, and the possibilities and range of applications of an OMFC technology is very large. From a practical viewpoint, molecular metal complexes that are soluble in different solvents and allow dispersion on very small surfaces, but are capable of delivering high power densities upon oxidation of alcohols and sugars, could indicate a way to the further miniaturization of fuel cells for biological applications and biosensors.[7,8,19–21] Molecular metal complexes can be easily embedded in a wide range of nanosized conductive supports, such as functionalized fullerenes, carbon nanotubes, nanofibers, and other nanosized matrices (such as titania nanotubes). The combination of a well-defined molecular architecture with a matching support might allow for the selective oxidation of polyalcohols into valuable chemicals under waste-free conditions, which is very difficult to achieve by traditional methods.

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