

DOI: 10.1002/cssc.201402316

Energy and Chemicals from the Selective Electrooxidation of Renewable Diols by Organometallic Fuel Cells

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Organometallic fuel cells catalyze the selective electrooxidation of renewable diols, simultaneously providing high power densities and chemicals of industrial importance. It is shown that the unique organometallic complex [Rh(OTf)(trop₂NH)(PPh₃)] employed as molecular active site in an anode of an OMFC selectively oxidizes a number of renewable diols, such as ethylene glycol, 1,2-propanediol (1,2-P), 1,3-propanediol (1,3-P), and 1,4-butanediol (1,4-B) to their corresponding mono-carboxylates. The electrochemical performance of this molecular catalyst is discussed, with the aim to achieve cogeneration of electricity and valuable chemicals in a highly selective electrooxidation from diol precursors.

Direct alcohol fuel cells (DAFCs) are the only devices where the free energy of alcohols can be converted into electrical energy with contemporaneous production of valuable chemicals. A crucial role in achieving this goal is played by the anode electrocatalyst, which must promote the selective oxidation of the alcohols to carboxylic compounds with fast kinetics. This goal can be achieved for a variety of renewable alcohols such as ethanol,^[1] ethylene glycol,^[2] glycerol,^[3] and sugars^[4] by means of innovative direct fuel cells, operating in an alkaline environment. In such devices, the anode electrocatalysts are generally based on nanometer-sized metal particles. Recently a number of molecular metal complexes have been shown to be active anode catalysts for alcohol electrooxidation. However, high overpotentials and low reaction rates make them unsuitable as anodes in DAFCs.^[5] In principle, molecular metal complexes should offer enormous advantages in the rational design and

optimization of anode electrocatalysts. In particular, a significant reduced metal loading on the electrode is expected because all metal sites are active, unlike catalysts based on metal nanoparticles. Recently, we have introduced a new type of DAFC, denoted as organometallic fuel cell (OMFC), operating in alkaline media, in which the anode catalyst is a molecular metal complex.^[6] In this device, the organometallic complex [Rh(OTf)(trop₂NH)(PPh₃)] (1) (Scheme 1) was shown to selectively catalyze the oxidation of ethanol to acetate. The efficiency of the OMFC was subsequently greatly improved by tuning the molecular architecture of the anode electrocatalyst and employing Ketjenblack EC 600 JD, a conductive carbon support having a high surface area of 1400 m² g⁻¹.^[7] This concept was taken up by other research groups which demonstrated that electrocatalysts based on specific metal complexes can oxidize alcohols^[8] and glucose^[9] at low overpotentials. In this paper, we show that the unique organometallic complex [Rh(OTf)(trop₂NH)(PPh₃)] (1)^[6] employed as molecular active site in an anode of an OMFC selectively oxidizes a number of renewable diols, such as ethylene glycol (EG), 1,2-propanediol (1,2-P), 1,3-propanediol (1,3-P) and 1,4-butanediol (1,4-B) to their corresponding monocarboxylates.^[10] We have investigated the electrochemical performance of this molecular catalyst, with the aim to achieve cogeneration of electricity and valuable chemicals in a highly selective electrooxidation from diol precursors.

The electrochemical activity of [Rh(OTf)(trop₂NH)(PPh₃)] deposited on Ketjenblack EC 600 JD, 1@C (Scheme 1), was first investigated by cyclic voltammetry at room temperature in deoxygenated 2 M aqueous KOH containing either 5 wt% EG, 1,2-P, 1,3-P or 1,4-B at a scan rate of 50 mV s⁻¹ (vs. RHE).

As expected, the CV response of 1@C in a 2 M KOH solution did not show any electrochemical activity up to the oxygen discharge potential (Figure 1, trace x). In contrast, a clear faradic current was observed starting at approximately 0.65 V (vs. RHE) when the electrolyte contained a mixture of a diol and 2 M KOH (Figure 1). The wide potential operating window (up to 1.2 V vs RHE) shows the inherent stability of the anode electrocatalyst at high potentials.



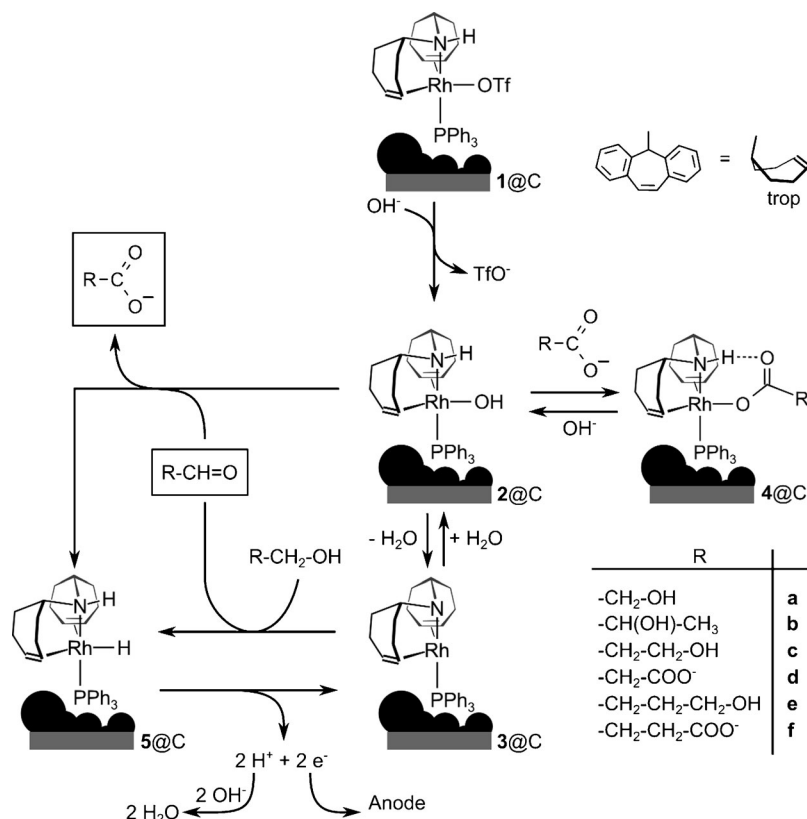
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Supporting Information for this article is available on the WWW under <http://dx.doi.org/10.1002/cssc.201402316>.



Scheme 1. Proposed mechanism for the reactions occurring on the anode of the OMFCs as described in detail in Ref. [6].

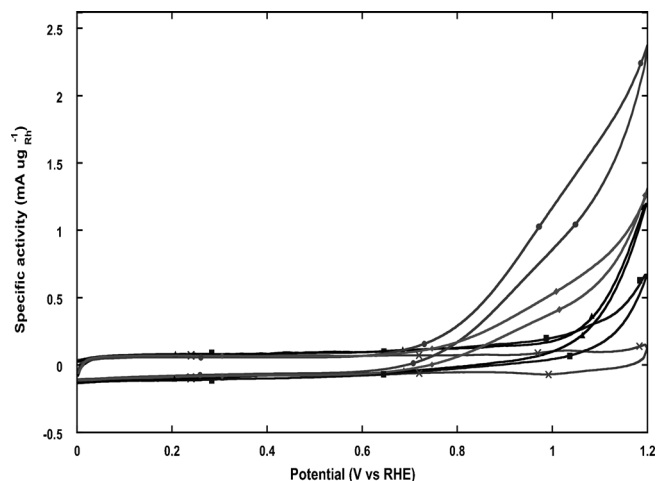


Figure 1. CV responses of a glassy carbon electrode coated with 1@C with: (●) 1,4-B; (◆) 1,3-P; (▲) 1,2-P; (■) EG; (×) 2 M KOH; aqueous solutions of diols (5 wt%) in 2 M KOH.

The specific activity ($\text{mA } \mu\text{g}^{-1}$ in Figure 1), increases with increasing the chain length of the diol. A similar trend was observed by Lamy et al. for the electrooxidation of polyalcohols in half cells on polycrystalline Pt and Au electrodes in alkaline media.^[11]

The membrane electrode assembly (MEAs) used for passive monoplanar air-breathing OMFCs were realized (as described

in the Supporting Information) using the anode 1@C on Ketjenblack EC 600 JD (ca. $0.8 \text{ mg}_{\text{Rh}} \text{ cm}^{-2}$). The potentiodynamic and power density curves shown in Figure 2 were obtained with water solutions of EG, 1,2-P, 2,3-P, and 1,4-B in 2 M KOH at room temperature. The cell containing 1,4-B exhibits the highest peak power density (8.5 mW cm^{-2} at 0.14 V) compared to the other diols (Figure 2a, Table 1).

The power density supplied by the OMFC fed with EG (2.7 mW cm^{-2} at 1.4 V, Figure 2a, Table 1) is lower than that observed with a traditional DAFC equipped with a palladium-based anode.^[2] No comparison can be made with DAFCs equipped with nanometer-sized metals as anodes fed with 1,2-P, 1,3-P, and 1,4-B simply because there are, at present, no data reported in the literature. In fact, the OMFCs described here are the first examples of direct alcohol fuel cells fed with these renewable diols.

For a broader comparison, other fuel cells based on molecular-catalyst anodes have been reported to deliver 24 mW cm^{-2} for a direct CO polymer electrolyte membrane fuel cell (PEMFC),^[12] $26 \mu\text{W cm}^{-2}$ for a H_2 PEMFC at 60°C ^[13] and 0.18 mW cm^{-2} for a direct glucose fuel cell,^[9] respectively.

The power density supplied by these OMFCs increases with cell temperature in active fuel cells (80°C fuel flow of 4 mL min^{-1} and an oxygen flow at the cathode of 0.2 L min^{-1}). Indeed, 12.4 mW cm^{-2} , 26.9 mW cm^{-2} , 24.3 mW cm^{-2} , and 42.2 mW cm^{-2} , were obtained with EG, 1,2-P, 1,3-P, and 1,4-B, respectively (Figure 2b, Table 1).

Galvanostatic experiments were performed at room temperature using passive cells in which the anode compartment was filled with solutions of the diols and KOH as electrolyte (Figure 3a). The fuel exhausts were quantitatively and qualitatively analyzed by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy and HPLC (see Supporting Information, Figure S1). The observed potential loss over time is due to the variation of fuel concentration during the galvanostatic experiments. The OMFCs fed with EG and 1,2-P, yielded selectively glycolate and lactate, respectively (Figure 3a, Table 1). To the best of our knowledge, the only selective oxidation of EG and 1,2-P to glycolate and lactate has been achieved with heterogeneous processes using Au and Pd catalysts.^[14] The galvanostatic experiment with 1,3-P gave 3-hydroxy-propanoate (92%) and malonate (8%) with a total conversion of 83%. Using 1,4-B, 4-hydroxy-butanoate (79%) and

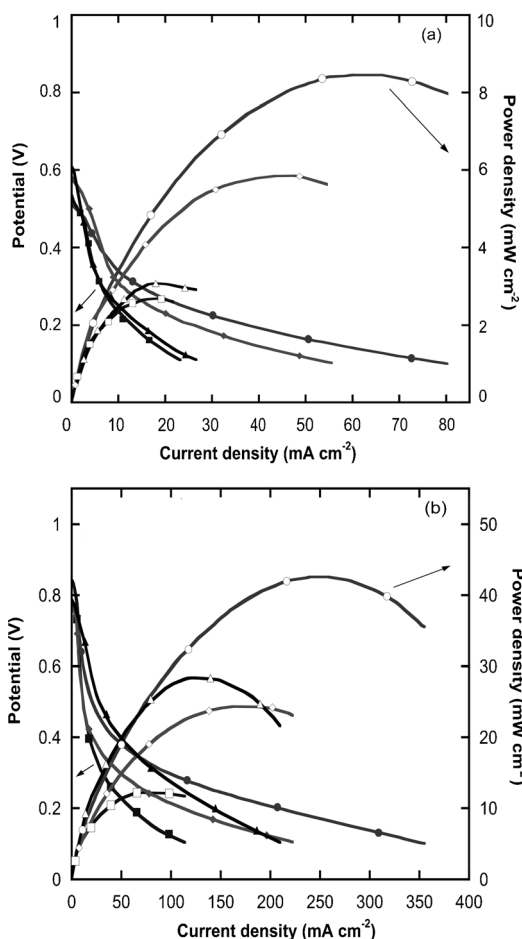


Figure 2. Polarization (filled symbols) and power density (open symbols) curves of OMFCs fueled with: (●) 1,4-B; (◆) 1,3-P; (▲) 1,2-P; (■) EG aqueous solutions 5 wt% in 2 M KOH. (a) Passive air-breathing OMFC at 22 °C and (b) active OMFC at 80 °C.

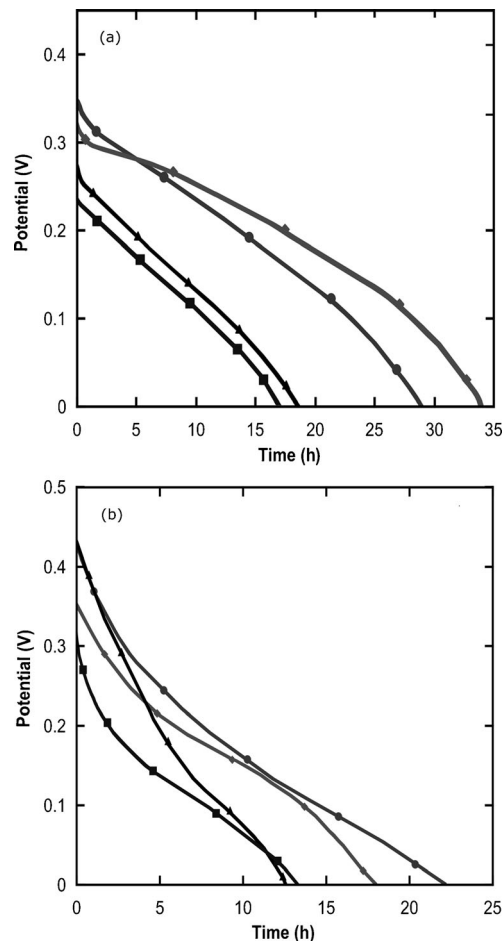


Figure 3. Galvanostatic curves of OMFCs at 20 mA, fueled with: (●) 1,4-B; (◆) 1,3-P; (▲) 1,2-P; (■) EG solutions 5 wt% in 2 M KOH; (a) air-breathing OMFC at 22 °C and (b) active OMFC at 80 °C.

succinate (21%) were obtained, with a total conversion of 79%. The selectivity of electrooxidation to the mono carboxylate remains high, but the oxidation of both alcohol groups also occurs, with the formation of both succinate and malonate (Table 1). From our observations, we conclude that both EG, containing two vicinal hydroxyl groups, as well as 1,2-P,

which contains both a primary and secondary vicinal hydroxyl group, undergo the electrooxidation of only one primary hydroxyl group. Diols with longer alkylene spacer chains such as 1,3-P and 1,4-B also undergo, to a small extent, the oxidation of both alcohol groups (Supporting Information, Scheme S1).

Galvanostatic experiments carried out at 80 °C showed a higher catalytic activity for the electrooxidation of all diols in terms of turnover number (TON) and energy released, while the selectivity remained substantially unaltered (Figure 3b, Table 1). At present, we assume that the different activity as well as the different selectivity of diols oxidation is due to both electronic and steric factors. For example, the longer chain length between the two alcohol groups in the diol tends to lead to some oxidation of both alcohols.

Table 1. Catalytic data for air breathing and active cell OMFCs.

Fuel	T [°C]	Max. power density [mW cm ⁻²]	TON	Conversion [%] ([mmol])	Galvanostatic time	Products
EG	22	2.7	86	38 (3.2)	17 h 14 min	100% glycolate
1,2-P	22	3.1	92	50 (3.4)	18 h 17 min	100% lactate
1,3-P	22	5.9	173	83 (6.1)	34 h 16 min	92% 3-hydroxy-propanate 8% malonate
1,4-B	22	8.5	114	78 (11.4)	28 h 38 min	79% 4-hydroxy-butanoate 21% succinate
EG	80	12.4	329	28 (12.1)	12 h 45 min	100% glycolate
1,2-P	80	26.9	318	34 (12.0)	12 h 39 min	100% lactate
1,3-P	80	24.3	445	45 (16.3)	17 h 29 min	96% 3-hydroxy-propanate 4% malonate
1,4-B	80	42.2	486	79 (18.4)	22 h 11 min	74% 4-hydroxy-butanoate 26% succinate

A series of experiments was performed in order to exclude the possibility that the remarkable electrocatalytic activity of 1@C is due to a decomposition of the organometallic complex during galvanostatic cycles to form active nanoparticles of Rh⁰. This is indeed not the case as: a) inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis of the anode exhausts after the galvanostatic experiments showed no rhodium leaching from the electrode into the solution; b) High resolution TEM (HR-TEM) analysis of the anode catalyst after several galvanostatic cycles with 1,2-P at 80 °C did not reveal traces of Rh⁰ nanoparticles and c) a Rh⁰/C catalyst synthesized with the same metal loading showed a poor activity and selectivity for electrooxidation of 1,3-P and 1,4-B.^[15]

In an attempt to gain further insight into the 1,3-P electrooxidation mechanism, a passive monoplanar OMFC was fed with a solution of 3-hydroxypropionic acid (5 wt%) and 2 M KOH. The cell peak power density output was 0.7 mWcm⁻² (Supporting Information, Figure S2). Quantitative and qualitative analysis of the fuel exhaust after a galvanostatic run showed the formation of malonate (Supporting Information, Figure S3, S4). This result clearly indicates that 3-hydroxy-propanoate as well as 4-hydroxy-butanoate can undergo 1@C-mediated electrooxidation leading to the di-carboxylate products malonate and succinate, respectively.

Model reactions in homogeneous solution were also performed to rationalize the electrocatalytic cycles. **1** reacted immediately with aqueous KOH solutions of EG or 1,2-P to give the hydride complex [Rh(H)(trop₂NH)(PPh₃)] (**5**), which reacted immediately with glycolic acid or lactic acid to quantitatively give the η¹-O-glycolate complex Rh(eq-OCOCH₂OH)(trop₂NH)(PPh₃) (**4a**) and the η¹-O-lactate complex [Rh(eq-OCOCH(OH)CH₃)(trop₂NH)(PPh₃)] (**4b**), respectively (Scheme 1).

The experimental findings reported in this paper support the mechanism which we already suggested for the catalytic electrooxidation of ethanol.^[6,7] Scheme 1 summarizes in strongly simplified form the key-findings obtained with diols. On the electrode surface, the precursor 1@C is rapidly converted into the hydroxo complex, [Rh(OH)(trop₂NH)(PPh₃)]@C (**2@C**), which is in a rapid equilibrium with the amide [Rh(trop₂N)(PPh₃)]@C (**3@C**) and water. The amide **3@C** dehydrogenates diols to aldehydes. Under the basic reaction conditions, the aldehydes are rapidly further converted promoted by catalyst **2@C** to form carboxylate ions and **5@C**. The latter complex is oxidized at the electrode, releasing two H⁺ (neutralized to give water under basic conditions) and two electrons with regeneration of the amide **3@C**.

In summary, our results demonstrate that OMFCs are indeed capable of providing simultaneously high power densities, which come close to those observed with noble metal particles,^[2] and chemicals of industrial importance by the highly selective oxidation of renewable diols.^[16] The catalytic electrooxidation of 1,4-B with 1@C in an active OMFC represents the benchmark with respect to activity and selectivity in these types of devices.

We believe that the concept of OMFCs is valid and offers an unprecedented flexibility. A wide range of possible combina-

tions of organometallic complexes and conducting support materials can be applied to produce, under waste-free conditions, chemicals which may be of industrial relevance.

Acknowledgements

The authors acknowledge the financial support from FIRB 2010 project RBFR10J4H7_002 and Ente Cassa di Risparmio Firenze for HYDROLAB2.

Keywords: carboxylates • energy conversion • organometallic fuel cell • oxidation • renewable alcohols • rhodium

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Received: April 16, 2014

Published online on July 31, 2014