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# Key issues to high electroactivity for methanol oxidation and oxygen reduction of Pt-based supported catalyst in fuel cells relevant environment

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## Abstract

In this work some of the key issues which affect the performance of catalysts for the anode and cathode electrodes in Direct Methanol Fuel Cells are analyzed. To deal with present challenges and overcome limitations different approaches have been implemented, which include catalyst support diversification and functionalization, control of particle size and the introduction of Pt alloying and heat treatment in order to enhance the rate of critical reactions such as CO electrooxidation and oxygen reduction reaction and also reduce Pt loading. A catalyst design strategy has been devised which incorporates the mentioned approaches in order to tackle various critical aspects for both electroactivity and stability, considered essential to boost Direct Methanol Fuel Cells technology.

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## 1. Introduction

Direct Methanol Fuel Cells (DMFCs) are electrochemical devices where methanol oxidation occurs to produce electricity and heat. Basically, the device is similar to a battery since it converts the chemical energy of fuel and oxidant into electric energy; yet unlike batteries, fuel cells do not need recharging: the fuel is continuously supplied to the anode and the oxidant to the cathode. Methanol oxidation occurs with the release of protons and electrons; the protons go through a conductive membrane to the cathode, where oxygen is introduced and reduced to form water; the electrons go through the external circuit and correspond to energy produced that can be converted into work. The main disadvantage is the release of CO<sub>2</sub> as the product of the methanol oxidation reaction (MOR). However, in a

sustainable energy future, the cells should be associated with carbon capture and recycling (CCR) technology, closing the loop of harmful emissions [1,2] with methanol being produced from renewable sources [3].

DMFCs have some advantages when compared to hydrogen fuel cells: methanol can be transported and store in liquid phase, using the infrastructure for liquid fuels already available [4,5]. This flexibility on fuel handling makes this technology not only attractive for large scale energy production and transportation, but well suited for small portable applications, for example in consumer electronic devices [4-8]. The DMFCs are projected to reach a market of USD 188.82 Million by 2020 [9]. The portable application market segment is expected to show the highest growth rate with DMFCs, called to fill in the gap between energy demand and energy storage capacity. The energy density of methanol is higher than that of hydrogen [8] and also of lithium ion batteries [6,7]. Apart from that, easy/short time refueling and cold

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start are considered substantial advantages driving DEMFCs technology development.

For the continuous market increase of DMFCs for portable applications, challenges include reducing noble metal catalyst loading for lower cost, reducing methanol crossover for increased efficiency, simplifying the BOP for increased energy and power density and improved reliability [8]. So far, the best catalysts are still based on supported Pt nanoparticles, which are prone to CO poisoning on the anode side [10–13]. On the cathodic side, the sluggishness of the oxygen reduction reaction (ORR) kinetics also demands catalysts with a more efficient chemical-to-electrical energy conversion to contribute to necessary improvements in cell performance and lifetime [14,15].

In this work some of the key issues which affect the performance of catalysts for the anode and cathode electrodes in DMFCs are analyzed. To deal with the mentioned challenges and overcome limitations different approaches have been implemented, which include catalyst support diversification and functionalization, control of particle size and the introduction of Pt alloying in order to enhance the rate of critical reactions in DMFCs such as CO electrooxidation (COR) and ORR and also to reduce Pt loading. A catalyst design strategy has been devised which incorporates the mentioned approaches in order to tackle various critical aspects for both electroactivity and stability, considered essential to boost DMFC technology.

## 2. Catalyst design

### 2.1. Introduction

Although the thermodynamic potential for the electro-oxidation of methanol in acid electrolytes is close to that of hydrogen oxidation, the overall reaction is very demanding due to the multi-electron transfer to form carbon dioxide. The half reaction is:



The generally accepted mechanism for the methanol oxidation reaction (MOR) on Pt catalysts proceeds with the electroadsorption of methanol, followed by proton and electron stripping. Dehydrogenation and insertion of oxygen into the adsorbed methanol fragment, as well as removing six electrons from each molecule are necessary for full oxidation. The transfer of electrons occurs in a step-wise manner, giving rise to the formation of surface adsorbed species which act as poisons for ensuing methanol adsorption and oxidation. Water is co-adsorbed

at neighboring sites to the bound CO and oxygen transfer occurs to give CO<sub>2</sub>, which desorbs from the catalyst surface. At potentials below ca. 0.45 V vs. RHE, the surface of Pt becomes poisoned with a near-monolayer coverage of CO and further adsorption of water or methanol cannot occur. Rapid decay of the current, as a result of the formation of strongly bound intermediates, is found for clean Pt surfaces which, initially, show very high activity for the MOR [4,5].

The development of advanced Pt-based catalysts has been focused, for some time, on the addition of a second metal (Ru, Sn, W, Re) able to provide adsorption sites capable of forming OH<sub>ads</sub> species, at low potentials, adjacent to poisoned Pt sites. The OH<sub>ads</sub> is then able to react with the bound CO to produce CO<sub>2</sub> and free sites for further methanol adsorption. For promoters such as Ru, stable methanol oxidation currents occur at significantly lower potentials (<0.25 V vs. RHE) than Pt. In this work enhancement of the catalytic activity of own produced Pt-Ru catalyst will be discussed in section 5. Regarding the ORR, mechanism pathways are briefly introduced, in section 6, for Pt and alternative Pt-based alloys with high selectivity, which may safeguard generation of water as the only by-product, stability and durability so that maximum power output in fuel cells is ensured.

More recent efforts have been focused on how to use platinum more effectively. In general, to achieve the maximum number of active sites of a given active phase, dispersion of that phase on an inert support is required. In the case of low-temperature fuel cells, the support is required to provide high surface area, high level of catalyst dispersion, facilitate electron transport during electrochemical reactions, porous structure for maximum fuel contact and product release. Also good electronic conductivity and corrosion resistance are paramount to maintain a good catalyst-support interaction and high stability in fuel cell environment [4,5]. These requirements are generally met by conductive carbon supports, which allow the active phase to be dispersed finely over the support surface. In this work, in the context of the mentioned requirements, Vulcan XC-72 and multi-walled carbon nanotubes (MWCNTs) are the catalyst supports of choice.

### 2.2. Support functionalization

As already stated, to achieve high efficiency and stability in DMFCs, catalysts, for both MOR and ORR, are prepared in the nanosized range and dispersed on high surface area carbon supports [4,5,16].

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