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# Methanol oxidation reaction on core-shell structured Ruthenium-Palladium nanoparticles: Relationship between structure and electrochemical behavior

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## HIGHLIGHTS

- Synthesis and physical evaluation of nanostructured Pd-Ru electrocatalysts.
- High electrocatalytic activity towards methanol oxidation for Ru@2Pd@Ru/C catalyst.
- Investigation of methanol oxidation reaction product distribution.
- CO<sub>2</sub> current efficiency over 90% for core-shell-terrace catalyst.

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## ABSTRACT

In this work the relationship between structural composition and electrochemical characteristics of Palladium(Pd)-Ruthenium(Ru) nanoparticles during alkaline methanol oxidation reaction is investigated. The comparative study of a standard alloyed and a precisely Ru-core-Pd-shell structured catalyst allows for a distinct investigation of the electronic effect and the bifunctional mechanism. Core-shell catalysts benefit from a strong electronic effect and an efficient Pd utilization. It is found that core-shell nanoparticles are highly active towards methanol oxidation reaction for potentials  $\geq 0.6$  V, whereas alloyed catalysts show higher current outputs in the lower potential range. However, differential electrochemical mass spectrometry (DEMS) experiments reveal that the methanol oxidation reaction on core-shell structured catalysts proceeds via the incomplete oxidation pathway yielding formaldehyde, formic acid or methyl formate. Contrary, the alloyed catalyst benefits from the Ru atoms at its surface. Those are found to be responsible for high methanol oxidation activity at lower potentials as well as for complete oxidation of CH<sub>3</sub>OH to CO<sub>2</sub> via the bifunctional mechanism. Based on these findings a new Ru-core-Pd-shell-Ru-terrace catalyst was synthesized, which combines the advantages of the core-shell structure and the alloy. This novel catalyst shows high methanol electrooxidation activity as well as excellent selectivity for the complete oxidation pathway.

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## 1. Introduction

During the last decades power devices which are run by alternative fuels have been of high research interest. Among others, research work is put in the further development of the alkaline direct methanol fuel cell (alkaline DMFC) technique. Compared to hydrogen driven fuel cells and other direct alcohol fuel cells, such as the direct ethylene glycol fuel cell or the acidic DMFC the alkaline utilization of methanol seems to be an acceptable compromise

between high energy density (liquid fuel) and faster reaction kinetics [1–5]. Besides this, the use of a liquid fuel also goes along with several benefits regarding its transportation, storage and refilling process. In addition, while bi-reforming of methane to methanol allows producing methanol in an economic and efficient way from a fossil source [6,7], latest research is concerned with producing methanol by reduction of CO<sub>2</sub>, which could lead to a potentially CO<sub>2</sub> neutral fuel [8,9].

With methanol being a potential candidate as fuel for future power units, alkaline DMFC technology has to overcome several issues for a successful commercialization. For example, the

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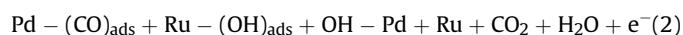
carbonation of hydroxide is considered to be a main drawback for anion-exchange membrane (AEM)-based fuel cells, because it leads to a loss of ionic conductivity leading to cell performance loss due to  $\text{CO}_2$  [10]. Besides this, carbonation potentially causes formation of a pH gradient between cathode and anode altering the enhanced electrode kinetics in alkaline environment [11]. On the material level, further improvements of alkaline DMFC technology concern the design of anion-conductive, highly stable polymers for the application as membrane [12] or binder material [13] and the development of a cheap, stable and highly active anode catalyst towards methanol oxidation reaction [14]. The latter was recently achieved by using Palladium (Pd)-based catalysts instead of Platinum (Pt). Even though Pd is only slightly cheaper than Pt, its activity towards methanol oxidation in alkaline media is strongly enhanced by mixing inexpensive, oxophilic metals like Ruthenium (Ru) to Pd. Besides high activity and stable behaviour, these catalysts show a significantly higher  $\text{CH}_3\text{OH}$ -to- $\text{CO}_2$  conversion efficiency than Pt resulting in a better utilization of the fuel [15]. Implementing Pd-based catalysts into alkaline DMFCs resulted in maximum power outputs of over  $0.1 \text{ W cm}^{-2}$  for overall Pt-free membrane electrode assemblies [15,16].

To further improve Pd-based anode catalysts for the alkaline DMFCs, understanding the methanol oxidation reaction mechanism is crucial.

The mechanism of the methanol oxidation on Pt or Pd surfaces has been intensely studied in alkaline media [17–21]. The very basic steps during the oxidation of  $\text{CH}_3\text{OH}$  are illustrated in Fig. 1 by the so-called dual-pathway characteristic [22]. After adsorption of the  $\text{CH}_3\text{OH}$  molecule onto the catalyst surface C-H bond dissociation is the initial step (under aqueous electrochemical conditions). The complete dehydrogenation of  $\text{CH}_3\text{OH}$  yields strongly adsorbed carbon monoxide ( $\text{CO}_{\text{ads}}$ ), as illustrated in the upper pathway. The lower pathway shows the incomplete oxidation yielding soluble intermediates: formaldehyde, formate and methyl formate. These products are able to diffuse into the bulk electrolyte or to re-adsorb onto the catalyst surface and further react to  $\text{CO}_2$ . The  $\text{CO}_2$  formed due to re-adsorption is often referred to as secondary  $\text{CO}_2$ .

Bagotzky et al. and Gilman et al. identified the adsorption of OH on the catalyst surface to play a key role in dehydrogenation as well as oxidation steps during methanol electrooxidation [17,19,23]. These studies showed, that complete oxidation of  $\text{CH}_3\text{OH}$  to  $\text{CO}_2$  requires a catalyst that does not only assist C-H bond scission but which also facilitates the dissociation of water molecules providing O-containing species on its surface. Those activated water molecules on the catalysts surface are from particular importance for removal of strongly bound  $\text{CO}_{\text{ads}}$ . This reaction step has been

attributed to be the rate determining step (rds) during methanol oxidation reaction in alkaline media for Pt [18] as well as for Pd [20,21] and proceeds through a Langmuir-Hinshelwood type reaction mechanism. Despite its general high methanol oxidation reaction activity, pure Pd catalysts exhibit a lack of enough O-containing species, especially at low oxidation potentials. This leads to a significant loss in catalytic activity due to  $\text{CO}$ -poisoning as well as insufficient conversion of  $\text{CH}_3\text{OH}$  to  $\text{CO}_2$  [15,16,20]. For the application as anodic fuel cell catalysts the complete oxidation of  $\text{CH}_3\text{OH}$  is of high importance. This is because oxidation to  $\text{CO}_2$  yields the maximum amount of 6 electrons per  $\text{CH}_3\text{OH}$  molecule, whereas oxidation to formaldehyde or (methyl) formate yields only 2 or 4 electrons, respectively, resulting in a lowered faraday efficiency. The problem of too few O-containing compounds on the Pd catalysts surface has successfully been addressed by alloying the electrocatalytic active metal with a second, more oxophilic one, such as Ru [15,24], Ni [25,26], Ag [20,27], Sn [28], Co [29], Rh [16] or In [30]. These catalysts showed significantly higher methanol electrooxidation activity where at the same time the content of the Pd metal was lowered. Especially Ru is a promising candidate as add-metal for bimetallic catalysts, because it leads to high activity, high  $\text{CO}_2$  current efficiency (CCE) and a significant cost reduction [15]. The influence of the co-catalytic component Ru can be described by two basic concepts. Firstly, Ru atoms alter the electronic properties of neighbored Pd atoms and cause strain on the Pd lattice [31]. This leads to more weakly bound adsorbents on the Pd surface; which facilitates both the  $\text{CO}_{\text{ads}}$  removal as well as dehydrogenation steps during methanol electrooxidation. This effect is called ligand or electronic effect. Secondly, Ru atoms which are present at the surface of the catalyst tend to adsorb oxygen containing species. The oxygen containing species facilitate the removal of  $\text{CO}_{\text{ads}}$  which are formed on adjacent Pd atoms. This, so-called bifunctional mechanism, takes place on Pd too, but Ru provides activated water compounds at lower potentials than Pd. The occurring reactions of the bifunctional mechanism are given in Equations (1) and (2).



However, the promoting effects of Ru are limited. Gasteiger et al. found that for different PtRu alloys the surface composition with a Ru content of approx. 10 at-% was the most active (depending on reaction conditions, investigations conducted in acidic environment) [32]. It was concluded that there is a minimum number of simultaneously accessible neighboring Pt sites needed for the dehydrogenation step. Further evidence for this geometric effect was published in 2005 by a Pt coverage dependent investigation of methanol and CO electro-oxidation on Pt sites generated via spontaneous deposition onto Au and Ru surfaces [33]. These investigations show that for an alloyed catalyst an optimum ratio of the two metals exists and that the active component for methanol electrooxidation cannot be decreased in an arbitrary manner without losing significant activity. This means that the electrochemical activity can be enhanced by incorporating Ru but the major part of those catalysts is still made up of expensive Pt metal. The same problem is transferable to mixed Pd-Ru catalysts. To further lower the cost of a Pd-Ru catalyst while maximizing the catalytic activity, modifying the nanostructure of the catalyst is necessary.

Beside alloyed catalysts, recent investigations on core-shell structured nanoparticles have shown beneficial catalytic features during different electrochemical applications such as CO-tolerant hydrogen oxidation reaction (HOR) catalysts [34–36] or highly active oxygen reduction reaction (ORR) catalysts [37,38]. A

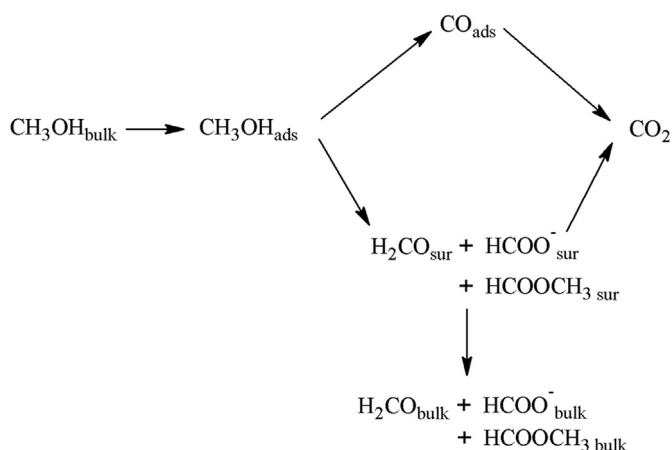


Fig. 1. Simplified reaction mechanism of the methanol oxidation on a platinum surface, showing the dual pathway characteristic, according to [22].

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