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Electrocatalytic activity and operational stability of electrodeposited Pd–Co films towards ethanol oxidation in alkaline electrolytes

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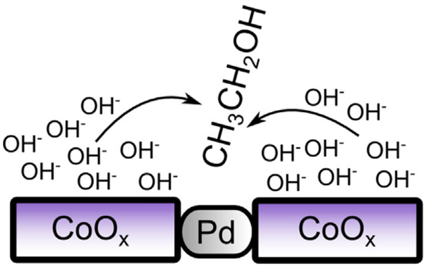
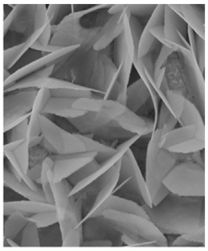
HIGHLIGHTS

- Pd–Co catalysts were electrodeposited with compositions between 20 and 80 at% Co.
- A transformation of alloyed Co to CoOOH/Co_3O_4 flakes was observed after cycling.
- The Co in the films supplies –OH to EtOH oxidation, reducing onset potential.
- A max peak current density is found at an optimum composition of 77 at% Co.
- A 50 at% Co–Pd film exhibited the highest stable currents among Pd–Co alloys.

GRAPHICAL ABSTRACT





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ABSTRACT

Direct alkaline ethanol fuel cells (DEFCs) are usually run with Pd anodic catalysts, but their performance can be improved by utilizing alloys of Pd and Co. The oxyphilic Co serves to supply ample –OH to the ethanol oxidation reaction, accelerating the rate limiting step at low overpotential under alkaline conditions. Pd–Co films with compositions between 20 and 80 at% Co can be prepared by electrodeposition from a NH_3 complexing electrolyte. Cyclic voltammetry studies show that the ethanol oxidation peak exhibits increasing current density with increasing Co content, reaching a maximum at 77% Co. In contrast, potentiostatic measurements under conditions closer to fuel cell operating conditions show that a 50 at% Co alloy has the highest performance. Importantly, the Co–Pd film is also found to undergo phase and morphological transformations during ethanol oxidation, resulting in a change from a compact film to high surface area flake-like structures containing Co_3O_4 and CoOOH; such a transformation instead is not observed when operating at a constant potential of 0.7 V_{RHE}.

1. Introduction

Direct Ethanol Fuel Cells (DEFCs) present various attractive features as power sources for portable and, more recently, transportation applications, since they exhibit energy densities

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comparable to gasoline and, in contrast to hydrogen, benefit from a simpler and mostly existing storage and transport infrastructure [1,2]. The use of ethanol, as well as other high molecular weight alcohols such as ethylene glycol or glycerol, is advantageous with respect to methanol or formic acid feeds, due to their low toxicity [3,4], and the possibility to produce these alcohols from biomass (sugar- or cellulose-based) using renewable, CO_2-neutral methods [5,6]. The main drawback of these devices however derives from the sluggish kinetics of ethanol oxidation, much slower than that of lighter alcohols or H_2, which results in lower efficiency and inferior performance with respect to the corresponding fuel cells. The development of efficient and selective anodic electrocatalysts is necessary to overcome this hurdle. These anodic electrocatalysts could also be successfully exploited in the electrochemical reforming of bio-alcohols providing a sustainable route for the co-generation of hydrogen and important raw chemicals [7–9].

Platinum catalysts are commonly used in acidic electrolytes because of their excellent ability to enhance the adsorption and dissociation of small organics molecules (SOMs); however, strongly adsorbed organic species such as carbonyl and CO, tend to poison the catalyst [1]. Furthermore, the high cost of Pt contributes significantly (~50%) to the total fuel cell stack cost. In contrast, in alkaline media the kinetics of ethanol oxidation is faster, and the adsorption strength of organic fragments is weaker. Importantly, less expensive electrocatalysts such as Pd can be used due to their stability in alkaline environments [10]. In an alkaline-type DEFC the reaction at the anode is targeted to be the complete oxidation of ethanol to CO_2 (1), accompanied by the reduction of oxygen at the cathode (2), leading to the overall reaction of ethanol "combustion" (3) [6].

$$CH_3CH_2OH + 16OH^- \rightarrow 2CO_3{}^{2-} + 11H_2O + 12e^- \tag{1}$$

$$3O_2 + 6H_2O + 12e^- \rightarrow 12OH^- \tag{2}$$

$$CH_3CH_2OH + 3O_2 + 4OH^- \rightarrow 5H_2O + 2CO_3{}^{2-} \tag{3}$$

Reaction (1) consists of a series of intermediate steps, whereby adsorbed ethanol is oxidized via hydrogen abstraction to acetaldehyde; the latter may subsequently be oxidized further to CO_2, if the C–C bond is broken, or transformed into a terminal acetate product (Fig. 1) [11,12]. The rate determining step in this reaction mechanism is the adsorption of hydroxyl (OH_{ads}) at low overpotential, or the removal of the adsorbed ethoxy (CH_3CO_{ads}) by adsorbed hydroxyl at higher potentials [13]. The overall reaction could be accelerated by addition of a more oxyphilic metal to Pt or Pd, which would enhance water dissociation and the formation of oxygenated species that become available for further oxidation to acetic acid. Most studied in this context are Ru and Sn, with the latter providing higher oxidation currents [14]; Co on the other hand could provide the same function at a lower cost with respect to Ru, while possibly enhancing C–C bond breaking, due to the homologous electronic structure to Rh and Ir, both known to enhance selectivity towards complete oxidation [14,15].

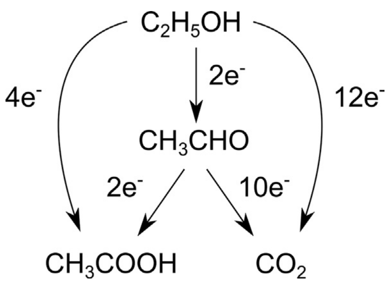

Fig. 1. Simplified reaction mechanism for ethanol oxidation; the reaction can either lead to CO_2 if the C–C bond is broken or end at acetate as a terminal product [11,12].

The overall selectivity for ethanol complete oxidation is found to be generally low, with the exception of Rao et al. [16], who reported a 55% CO_2 conversion efficiency in alkaline solutions and only 2% in acidic ones. CH_3COO^- is in most cases by far the major product of ethanol oxidation in alkaline environment, decreasing the faradaic efficiency by 1/3 as compared to carbonate formation. Despite this intrinsic loss of faradaic efficiency, the fast kinetics of acetate production on Pd results in relatively low anodic overpotential, providing DEFCs with power densities up to 335 mW cm^{-2} [17,18].

Pd-Ni [19–22] and Pd–Co [23–25] have been already investigated as anodic catalysts for alkaline DEFCs, each showing better performance than Pd alone when normalized per unit area. The alkaline environment allows complete elimination of Pt from these fuel cells. Indeed in alkaline environment iron and cobalt macrocycles are active for the oxygen reduction with similar performance to Pt based ORR catalysts, these materials being also inactive toward alcohol oxidation This is particularly relevant as it results in negligible voltage drop for alcohol crossover [26].

The studies referred to above speculate that the facilitated formation of –OH on the 3d transition metal in alkaline solutions is the main mechanism by which ethanol oxidation was enhanced. Liu et al. identified the equiatomic composition to be optimum for formic acid and methanol oxidation at Pd–Co nanoparticles supported on carbon fibers [25]. Xu et al. mixed Pd nanoparticles 6–10 nm with oxides of Ce, Ni, Co, and Mn, and found that a Co_3O_4–Pd composite with an oxide content of 0.05 mg cm^{-2} yields the highest peak oxidation current for ethanol oxidation, while noting low stability for this oxide-Pd pairing [24]. So far however, the optimum features of the catalyst structure and composition for ethanol oxidation have not been assessed; in addition, the stability of the catalyst surface has received little to no attention. On a related issue, a rigorous protocol for the evaluation of the electrocatalytic activity in ethanol oxidation catalysts has been missing and current methods to compare catalyst activity are not standardized, hindering an accurate ranking of the relative activity of various catalysts.

In this work, we report on the electrocatalytic activity and long-term stability of Pd–Co alloy films in view of their potential application as anodic catalysts for alkaline DEFCs. We produce a set of thin film electrodes with a broad range of compositions, using electroplating from an ammonia-based electrolyte, and we evaluate different methods to rank activity towards ethanol oxidation. In the process, we identify an optimum alloy composition at a Co fraction around 50–60%, yielding the highest current densities for ethanol oxidation and also find that the reaction onset occurs at more negative potentials with increasing Co fraction. Accelerated oxidation of Co in the alloy to form Co (hydro)oxides is observed during the potential cycling of Pd–Co in alkaline, ethanol-containing electrolytes, which is accompanied by a morphological transformation to a high surface area flake-like structure, never explicitly reported before.

2. Experimental

2.1. Electrodeposition of Pd–Co

An ammonia-based complexing electrolyte was utilized in order to shift the redox potentials of the two metals closer together and thus facilitate the formation of alloy solid solutions [27]. The electrolyte was prepared as follows: first, two beakers were prepared, one containing a 20 mM $PdCl_2$, 0.4 M $(NH_4)_2SO_4$ and 0.5 M NH_3