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Novel Nanoscale Ceria–Platinum Composite Electrodes for Direct Alcohol Electro-Oxidation

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Abstract A nanocrystalline Pt/CeO_2 composite electrode is fabricated to study the electrochemical oxidation of methanol and ethanol. Three different methods have been developed for the preparation of the composite electrode and are compared in terms of their oxidation efficiencies. In general, all the electrode preparation methodologies show a great enhancement of the oxidation current for the alcohol. However, methods based on the electrodeposition of a ceria rich Pt matrix show the greatest effectiveness of alcohol oxidation. The enhancement of the anodic current is dependent on the particle loading and size distribution in the composite matrix. In general, ceria appears to be an effective alternative to ruthenium in direct alcohol fuel cells.

Keywords Direct alcohol fuel cells · Ceria · Oxidation · Catalysis · Electrochemistry · Methanol

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1 Introduction

Over the past several years there has been a growing concern about finding alternative sources of energy to replace our current fossil fuel dependency, both for environmental reasons and because of the low availability of fossil fuels [1–4]. The area of polymer electrolyte membrane (PEM) fuel cells has attracted a great deal of attention as a novel alternative to power small devices in transportation, communications and consumer electronics [3, 5]. However, the requirement of fuel reforming greatly hinders the performance of the fuel cells [6, 7]. In order to circumvent such requirement, direct alcohol-based fuel cells (DAFCs) have been strongly pursued as a promising alternative. The DAFC is in general a PEM fuel cell in which the alcohol is directly fed into the anode without the requirement of a fuel reformer [3]. The simplicity of the DAFCs has been shown with methanol [8–13] and ethanol [14–20] as well as with other small alcohols and carbohydrates [21]. Although DAFCs offer great promise, they also show several drawbacks. Several limitations of the DAFCs are the slow dynamics of alcohol oxidation, the alcohol crossover across the membrane, the durability and performance of the membrane and the stability and ease of poisoning the anode [3, 22–25].

The most common alcohol for DAFCs is methanol (Direct Methanol Fuel Cells, DMFCs), although ethanol has been recently gaining considerable attention due to its greater availability and higher energy storage capacity (per volume) than methanol [19, 21]. The best performing anode material for the electrochemical oxidation of methanol is platinum, whose high cost puts a great economic challenge into the DAFC design. Moreover, a common byproduct of the electrochemical oxidation of alcohols is carbon monoxide [22, 23]. Carbon monoxide is a result of the incomplete oxidation of the methanol as it is desired to be fully oxidized into carbon dioxide. Unfortunately, carbon monoxide binds very strongly to the platinum anode, poisoning the electrode and requiring very high overpotentials for the removal of the carbon monoxide. Such high overpotentials drop the overall performance of the cell and can be translated into a more expensive operation of the cell, reducing the cost benefits.

Recent fuel cell developments have found that the utilization of electrodes that are composed of Pt as a major component, but which contain mixtures of other metals, metal–oxides and non-metals can have enhanced catalytic properties toward methanol oxidation. Of these alternatives, Pt–Ru and Pt–Ru/C electrodes are commonly employed to enhance the oxidation of the alcohol via the well studied bifunctional mechanism [26–28]. The need to convert CO into CO_2 for the complete electrochemical oxidation of the alcohol and in order to minimize the poisoning has promoted the use of metal oxide electrodes as a replacement for Pt/Ru. The choice of oxide material and its role in catalysis is of paramount importance. Generally in catalysis, there has been a great interest in ceria (CeO_2) as a catalyst material [29, 30]. CeO_2 has shown a great ability to store and release oxygen (namely, the oxygen carrying capacity) without much distortion in the CeO_2 crystal lattice, as the cerium atom reversibly undergoes oxidation/reduction processes from Ce^{4+} to Ce^{3+}. Due to its oxygen carrying capacity, ceria has been used in catalysis, being often applied in the automobile's catalytic converter and for their use in the water–gas shift reaction. The ability to release oxygen reversibly can also be explored for the oxidation of adsorbed CO in DAFCs [31, 32]. In this work, several Pt/ceria composite electrodes have been prepared and their performance has been studied towards the electrochemical oxidation of methanol and ethanol. The performance of such electrodes with novel anode materials for DAFCs rival that of the Pt–Ru bifunctional catalyst and are worthy of further characterization.

2 Experimental

2.1 Reagents

Triply distilled water with 18 MΩ cm resistivity (Barnstead B-pure) was used to prepare all aqueous solutions. All chemicals were used as received. Methanol (Fisher, Anhydrous, ACS Reagent Grade) and Ethanol (Fisher, Anhydrous, ACS Reagent Grade) were used to prepare alcohol solutions of desired concentrations in 0.5 M H_2SO_4 (Fisher, ACS reagent grade) as supporting electrolyte. Electrochemical solutions were purged using high purity N_2 (Air Liquid) in order to remove excess dissolved oxygen. Concentrated HNO_3 (Fisher, ACS reagent grade) was used to clean the Pt electrodes. A Nafion 117 alcoholic solution (Fluka, purum in a mixture of aliphatic alcohols) was used to prepare the membrane material in the Nafion modified electrodes. High purity potassium hexachloroplatinate (Aldrich) was used for Pt electrodeposition. Ceria (cerium oxide) nanoparticles were obtained from published procedures and from Aldrich.

2.2 Methods and Apparatus

A three electrode apparatus was used in all electrochemistry experiments. Polycrystalline, 2 mm diameter Pt (CH Instruments, Inc.), Ag/AgCl (CH Instruments, Inc.) and Pt wire (CH Instruments, Inc.) electrodes were used as working, reference and counter electrodes, respectively, for cyclic voltammetry and electrodeposition experiments. Cyclic Voltammetry, CV, experiments were carried out on a CH Instruments Model 760C (CH Instruments, Inc. Austin, TX) potentiostat, without regard for liquid junction. A custom made 50 mL cell was used for the experiments. The working electrode was polished by circular rotation on a Buehler Microcloth polishing cloth, using Buehler 1 micron diamond polishing compound and Buehler Methadi fluid extender (Buehler, LTD, Lake Bluff, IL). The working electrode was then rinsed and cleaned in concentrated HNO_3 (Fisher, ACS reagent grade) for 30 min and the cleanliness of the Pt surface was ascertained by looking at the cyclic voltammetry of the electrode in a 0.5 M H_2SO_4 solution. The solutions were purged with N_2 for 10 min prior to experiments.

2.3 Preparation of Modified Electrodes

Ceria modified electrodes were prepared by one of three different methods: (a) immersion in a ceria suspension, (b) evaporation of a drop of the ceria suspension followed by coating of the electrode by the evaporation of a drop of an alcoholic solution of Nafion 117 and by (c) electrodeposition of Pt from a nano ceria suspended, potassium hexacholoroplatinate solution.

The composite electrodes prepared by immersion were placed in a 5 mM suspension of ceria nanoparticles for 12 h. The ceria nanoparticles were synthesized following published procedures [33]. The modified electrodes were then thoroughly rinsed with triply DI water and air dried prior to electrochemical experiments. The electrodes prepared by evaporation were prepared by placing a drop of the 5 mM ceria suspension used in the immersion procedure and allowed to air-dry for 12 h. This was followed by placing a drop of a 5% Nafion 117 solution in aliphatic alcohols (as commercially available). The Nafion solution is allowed to air-dry and the electrode is rinsed with triply DI water.

The composite electrodes modified by electrodeposition were prepared by the reduction of a K_2PtCl_6 solution using a Princeton Applied Research PAR-273 potentiostat (AMETEK, Princeton Applied Research). The electrodeposition of platinum for the formation of Pt/ceria composite electrodes was accomplished by holding the potential at –0.200 V vs. Ag/AgCl for 600 s while stirring the solution at rotations close to 200 rpm using a Corning PC-351 magnetic stirrer/hotplate, in a slight variation of previously published results [31]. The rate of electrodeposition was kept constant by looking at the current while depositing and adjusting the potential accordingly in order to keep the current constant.

In all cases, the cleanliness and suitability of the electrode prior to any electrochemical oxidation of the alcohols was ascertained by looking at the cyclic voltammetry of a 0.5 M H_2SO_4 solution using the desired electrode. All cyclic voltammetry experiments were carried at a scan rate of 100 mV/s unless specified. Moreover, the currents observed for the hydrogen adsorption regions of the voltammogram were used for normalization of the electroactive surface area of the electrodes after modification.

3 Results and Discussion

3.1 Electrochemical Oxidation of Methanol on Bare Pt Electrodes in 0.5 M H_2SO_4 and on Ceria Modified Electrodes via Immersion Into Ceria Suspension

Cyclic voltammograms for the Pt electrode prepared by immersion of a clean Pt electrode with a 5 mM ceria suspension showed an increased anodic current for the electrochemical oxidation of methanol as compared to the bare Pt electrode (see Fig. 1). The current observed for the oxidation of methanol on the modified electrode was significantly higher, with currents about two times greater than for the unmodified Pt electrode. When comparing the cyclic voltammogram of the ceria coated (by immersion) electrode to the clean, bare Pt in 0.5 M H_2SO_4, no noticeable difference in the hydrogen adsorption regions of the voltammogram were observed. This demonstrates that no noticeable change on the electrode's active Pt surface area is created by the surface modification using ceria. Therefore, such increase in the current can be attributed to a catalytic enhancement of the ceria nanoparticles towards the electrochemical oxidation of the methanol. Moreover, no noticeable shift in the onset potential for the methanol oxidation was observed on the cyclic voltammetry of the electrode modified with the ceria catalyst. In fact, a slightly lower (although, within the experimental error) onset potential for the oxidation of methanol was observed for the modified electrode. Not requiring a higher onset potential can be regarded as an indication of the catalytic enhancement of the ceria nanoparticles. However, due to the limited solubility of the ceria nanoparticles, a detailed measurement of surface coverage by the ceria nanoparticles was not possible. The adsorption of ceria nanoparticles from organic solvents such as benzene was attempted; however this resulted in further poisoning of the Pt electrode by competing adsorption of the organic solvent on the Pt surface. The coating of platinum by immersion from aqueous solution of ceria is an extremely slow process due to the limited solubility of the ceria nanoparticles. Finally, the catalytic enhancement of the ceria nanoparticles appears to be dependent on the aging of the nanoparticles in the solution. Freshly prepared nanoparticles show the aforementioned two-fold increase in the current, whereas, ceria particle suspensions prepared and aged for over 3 weeks do not show the increased oxidation current. Such behavior is currently under further study, but appears to be due to possible clustering of particles, increasing the average size of the particles, or due to a change of the Ce^{4+}/Ce^{3+} ratio when exposed to the environment, changing the oxygen buffering.

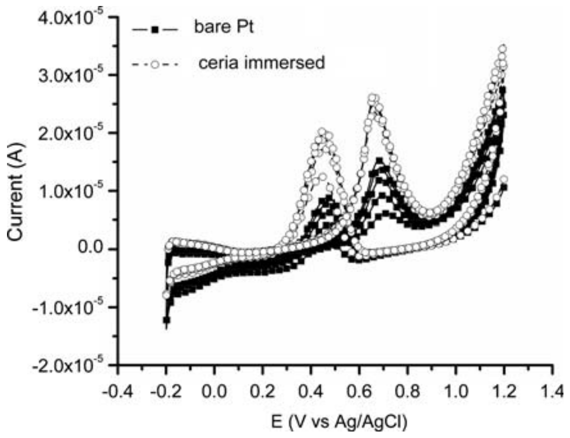


Fig. 1 Cyclic voltammetry of methanol electro-oxidation on a ceria immersed Pt electrode compared to the same, clean and unmodified electrode. A two-fold increase on the methanol oxidation current is observed, while the potential for the oxidation has an almost undifferentiable lower value

3.2 Methanol Electro-Oxidation on Nanoceria Modified Electrodes by the Drop Technique

The low solubility of the ceria in aqueous media is one of the limiting factors for obtaining a high particle loading on the electrode surface. In order to increase the ceria loading on the electrode surface, the electrodes were also prepared by evaporating the drop of the ceria suspension on top of the clean Pt electrode. After the drop evaporated, a drop of an alcoholic Nafion 117 solution was placed followed by air-drying. The Nafion 117 was used in order to immobilize the physisorbed ceria particles and in order to increase the conductivity of the ceria coating. As seen from Fig. 2 the electrode modified by evaporation of a ceria suspension shows a current of one order of magnitude higher than that of the electrode modified by immersion and almost 20 times higher than those of the bare Pt electrode. In the case of the electrode modified by evaporation, a very small increase in the overpotential for the electrochemical oxidation was observed. Such an increase is possibly due to a lower electrical conductivity of the ceria as compared to the bare Pt. The effect was not observed at lower ceria loads such as the immersion prepared electrode, but can be observed with increasing the ceria load. Such effects as well as a detailed study on the ceria load on the electrode are currently under study by electrochemical impedance spectroscopy (EIS).

3.3 Methanol Electro-Oxidation on Nanoceria Modified Electrodes Prepared by Electrodeposition of a CeO_2/Pt Composite

Alternatively, other methods can be utilized for the preparation of the composite electrodes. A simple, yet effective alternative to the modification of the electrode is based on published results by Campos et al. [31], but utilizing the nanoceria particles synthesized by our laboratories [33]. Modification of Pt electrode was realized by co-deposition from a 1.0 mM K_2PtCl_6 solution that also contained a 20 mM suspension of ceria nanoparticles. The modified electrode shows a very large increase in the catalytic current for the oxidation of methanol. The oxidation current exhibited was well over two orders of magnitude higher than the next-best performing electrode, which was prepared via evaporation of the ceria suspension, and nearly four orders of magnitude higher than the current observed for the bare electrode. However, caution must be exercised in the interpretation of such results, as the electrodeposition process causes an increase in the electrode's surface area. The changes in the surface area were normalized in order to account for the larger area of electrode that is exposed to the solution. Normalization of the electrode surface area was carried by observing the current for the hydrogen adsorption region. It would be ideal to be able to compare the performance of the different electrodes based on the Pt and ceria loading of the electrodes. However, without full information of the morphology of the electrode, we have to base our analysis on the active Pt surface area exposed to the alcohol solution. Based on such normalization, the current for the electrodeposited film was slightly over two orders of magnitude higher (insert in Fig. 3). By normalizing both the electrodes for the correct electrochemically active surface area, the value still show three orders of magnitude increase on the oxidation current. These results from the normalized current values point to a large catalytic enhancement by the nanoceria modified platinum electrode. The ceria modified electrode via electrodeposition was also prepared using different concentrations of ceria in the suspension, while keeping the K_2PtCl_6 concentration fixed at 1 mM, in order to vary the ceria load in the electrode. The currents obtained were similar in all cases, pointing that only a small amount of ceria is required and it is largely independent of the moderate ceria concentration in the studied range. Figure 4 shows that the current increases significantly as the methanol concentration is increased. The large currents observed are a food indication of the catalytic enhancement for the oxidation of the methanol, considering that more current is being generated per unit area. This increase in the current may imply that (1) CO poisoning is reduced, leaving more free Pt sites available to the oxidation of the alcohol, improving the electrode's turnover rate or that (2) among the different intermediate pathways of methanol oxidation, the rate for the complete six electron oxidation of the alcohol is increased. Other observations include that the oxidation current does not show a great deal of saturation, reinforcing the idea of the modified electrode having an increased ability to oxidize the alcohol and not be adversely affected by CO poisoning. A final observation is that an increase in

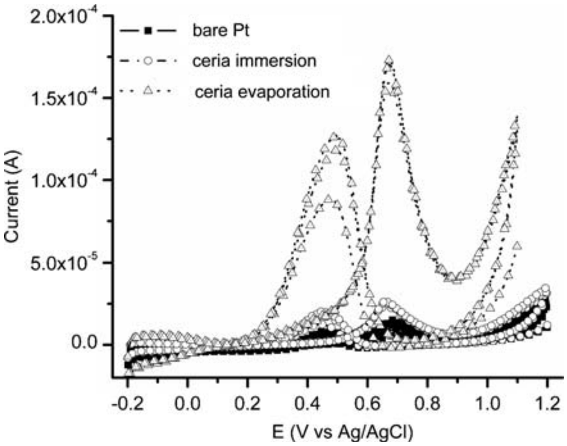


Fig. 2 Comparison of the electrochemical oxidation current of a bare Pt electrode to the enhanced current observed for an electrode modified by evaporation of a ceria suspension. A one order of magnitude increase in the current for electrode modified via ceria evaporation over that of the bare Pt is observed. A small increase in the overpotential for the oxidation is also observed

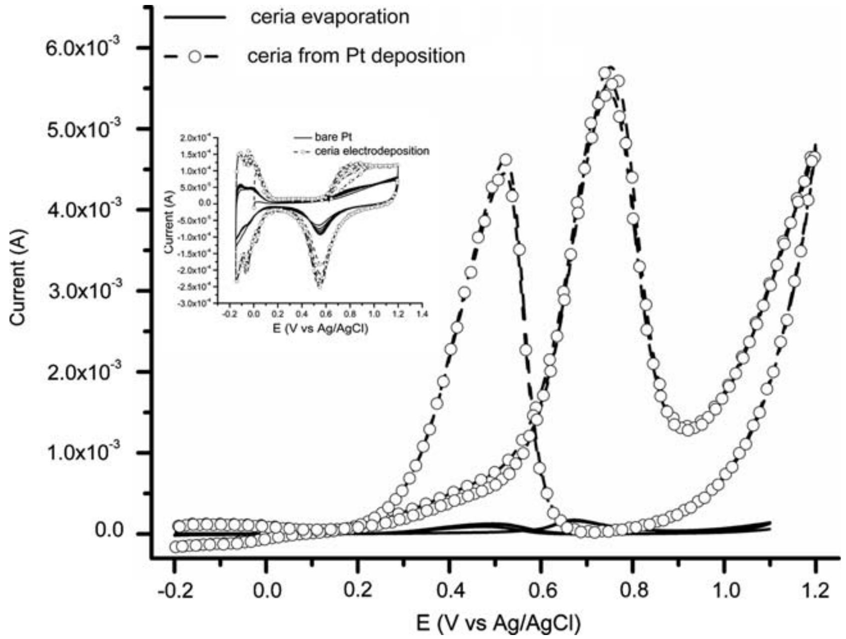


Fig. 3 Comparison of the electrochemical oxidation current for the electrode modified by ceria electrodeposition over that of the electrode modified via evaporation. An increase of around 50 times higher oxidation current without normalization for surface area is observed, or an increase of about 10 times higher current after normalization for surface area (insert: Cyclic voltammograms of the platinum electrode in 0.5 M H_2SO_4 solution prior (bare Pt) to the ceria modification, and after the ceria/Pt electrodeposition. A threefold increase in the surface area can be inferred from the surface adsorption peaks of the voltammogram, showing the increase of the electrochemically active surface area for the modified electrode. Such values can be used to normalize the electrode's performance due to surface area)

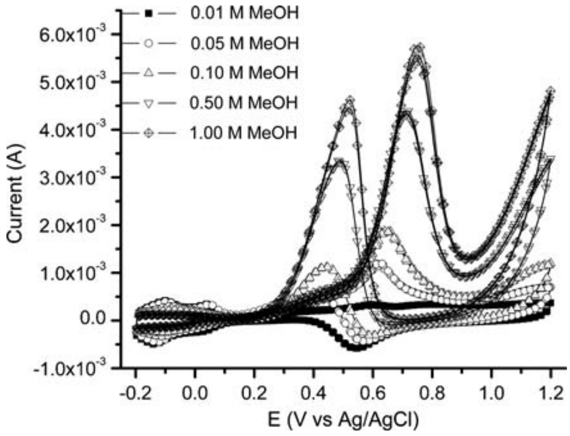


Fig. 4 Cyclic voltammograms of different concentrations of methanol on the ceria modified electrode by electrodeposition. It can be observed that in the 0.01–1.0 M methanol concentration range the electrode is not saturated

the onset potential required for the oxidation of the alcohol is observed in the electrodes modified by electrodeposition, and that in general, the larger the increase in the electrochemical oxidation current observed is associated with a larger increase in the onset potential needed for the oxidation. This increase in the onset potential also seems to also correlate with the higher ceria loads on the electrode and can possibly be attributed to the decrease in electrical conductivity of the ceria modified electrode as opposed to the bare Pt electrode. Experiments to accurately assess the load of ceria on the electrode are currently being pursued.

3.4 Electrochemical Oxidation of Ethanol on Ceria Modified Electrodes

Ethanol can be a more efficient and safer alternative to methanol in fuel cells, and its easy availability from agricultural or biomass products, makes it an ideal candidate for fuel cells. However, the electrochemical oxidation of ethanol is a challenging process with many intermediates and requiring different, more enhanced catalysts for the oxidation of the ethanol.

Figure 5 shows the cyclic voltammetry for different ethanol solutions and it can be readily observed that the ceria modified electrodes also offer a feasible alternative for the oxidation of ethanol. The overall current is lower than that of similar methanol concentrations, as can be observed from Fig. 6, but the response shows no loss of linearity and a relatively high current as well. The electrochemical oxidation of ethanol showed an increase in current as a function of alcohol concentration, with a smaller increase on the onset potential for the oxidation as the concentration increases. This observation may suggest

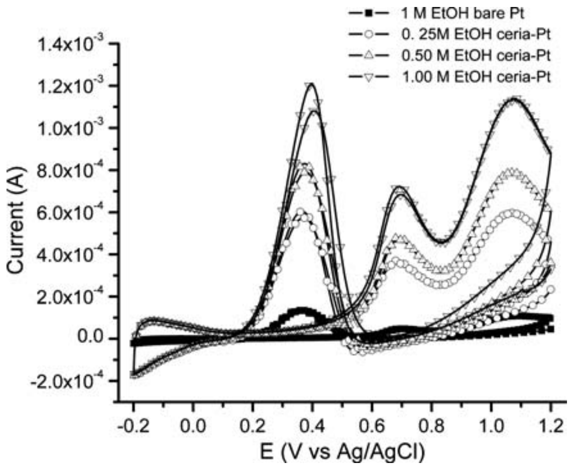


Fig. 5 Cyclic voltammograms of different concentrations of ethanol on the ceria modified electrode by electrodeposition. It can be observed that in the 0.01–1.0 M ethanol concentration range the electrode is not saturated. An extra oxidation peak is observed on ethanol, possibly due to the oxidation of intermediates produced in the oxidation

the presence of a lesser degree of carbon monoxide poisoning for the case of ethanol. Also, the oxidation of ethanol showed an additional oxidation peak at around 1.0 V vs. Ag/AgCl, which can explain the relative reduction of the current compared to the oxidation current obtained for methanol. The electrochemical oxidation of ethanol is believed to prefer a 2-electron oxidation to acetaldehyde or a 4-electron oxidation to acetic acid instead of the complete, 12-electron oxidation to carbon dioxide. In fact, it has been shown that for the electrochemical oxidation of ethanol, both acetaldehyde and acetic acid are generated [17, 34] and recent studies suggest that the formation of acetaldehyde is actually 600 times faster [35]. The voltammetric peak observed at positive potentials around 1.0 V vs. Ag/AgCl is associated with the desorption of species such as the acetic acid [36]. From Fig. 6 we can observe about a five-fold decrease in the oxidation current for ethanol as opposed to methanol for similar concentrations. The results necessitate a full catalytic study of the effect of the ceria loading on electrodes. The results may suggest that the kinetics for the ethanol oxidation are slower than those of methanol due to the formation of many intermediates, or that methanol is more easily poisoned by CO as a byproduct. Such results are currently under study.

4 Discussion

4.1 Mechanism for Oxidation of Methanol

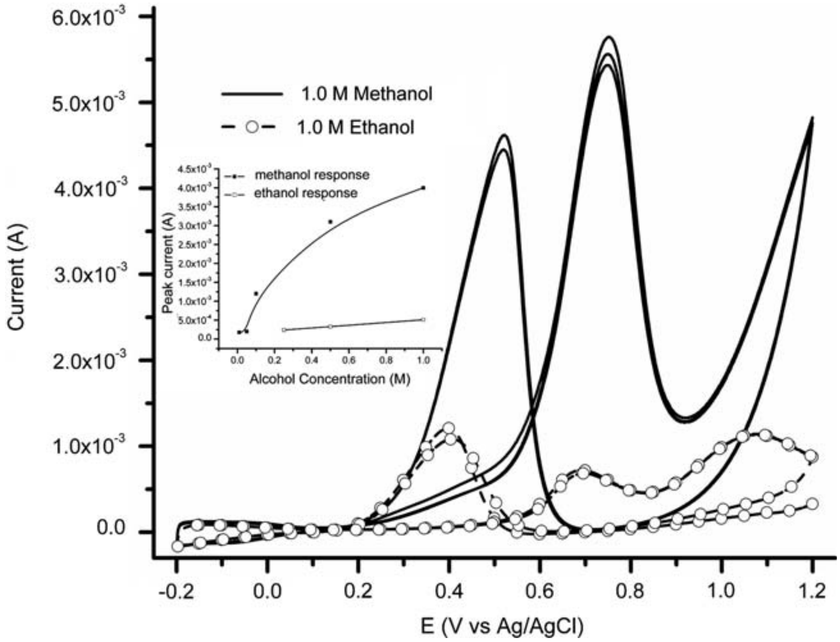
The anodic oxidation of methanol on platinum electrodes in DAFCs is usually believed to happen by a mechanism in which methanol is oxidized to CO, which is rapidly adsorbed on the Pt surface, followed by the slow, rate-limiting oxidation of the adsorbed CO to CO_2.

$$\begin{aligned} CH_3OH + H_2O \;\rightarrow\; & \text{Pt - CO}_{ads} + 4\ H^+ \\ & + 4\ e^-\ \text{(poison, CO adsorption)} \end{aligned} \tag{1}$$

$$\begin{aligned} \text{Pt - CO}_{ads} + H_2O \;\rightarrow\; & \text{Pt} + CO_2 + 2\ H^+ \\ & + 2\ e^-\text{(rate limiting)} \end{aligned} \tag{2}$$

The overall chemical reaction is a 6 electron process given by:

Fig. 6 Comparison of the electrochemical oxidation currents for 1.0 M methanol and 1.0 M ethanol solutions. It is observed that methanol yields a five times higher current, showing that the electrochemical oxidation is more feasible than that of methanol at the current catalyst (insert: Oxidation peak current as a function of the methanol and ethanol concentrations for the electrodes prepared by electrodeposition. It can be observed that only at the higher methanol concentrations the signal loses linearity and some saturation is observed. Such non-linearity can be due to the CO adsorption and poisoning of the electrode and it is not observed for ethanol)



$$CH_3OH + H_2O \rightarrow CO_2 + 6\ H^+ + 6\ e^- \tag{3}$$

The enhancement of the oxidation as assisted by ceria can be described to happen by any or both new possibilities: chemical enhancement of the oxidation of the adsorbed CO as assisted by ceria as an oxidation catalyst/oxygen donor, or by the effect of ceria's altering the electrode's morphology, physically inhibiting the CO adsorption. A mechanism for ceria's proposed enhancement of xidation can be described by the following reactions:

$$2CeO_2 + 2H^+ + 2e^- \rightleftharpoons Ce_2O_3 + 2H_2O \tag{4}$$

$$\begin{aligned} &Pt - CO_{ads} + 2CeO_2 + 2H^+ + 2e^- \\ &\quad \rightleftharpoons Ce_2O_3 + Pt + CO_2 + H_2O \end{aligned} \tag{5}$$

which assist on the weakening of the Pt–CO bond, thus reducing the CO poisoning effect and promoting the oxidation of the alcohol.

4.2 Mechanism for Oxidation of Ethanol

A similar mechanism can be described for the electrochemical oxidation of ethanol. Ethanol electro-oxidation involves a total of 12 electrons and several intermediate steps. In the electrochemical oxidation of ethanol, it is observed that the tow electron oxidation into acetaldehyde and the 4-electron oxidation into acetic acid are favored. It has been suggested that the first of these steps involves the dehydrogenation of the alcohol [35] into acetaldehyde via the following reactions:

$$CH_3CH_2OH \rightarrow CH_3COH + 2\ H^+ + 2\ e^- \tag{6}$$

$$CH_3COH + Pt_{(s)} \rightarrow Pt\text{ - }CH_3COH_{ads} \tag{7}$$

The process for the formation of acetaldehyde competes with the oxidation of the alcohol into acetic acid via a four electron oxidation,

$$\begin{aligned} &2\ CH_3CH_2OH + Pt_{(s)} + 4\ CeO_2 \\ &\rightarrow 2\ Ce_2O_3 + 2\ Pt\text{ - }CH_3COOH + 4\ H^+ + 4e^- \end{aligned} \tag{8}$$

The adsorption of acetic acid poisons the electrode and the desorption of the acid requires a very high onset potential, evidenced by the voltammetric peak at 1 V in Fig. 5. This process competes with the oxidation of the alcohol directly into CO_2 via the 12-electron oxidation reaction. A 12-electron process is rather non-trivial and the incomplete oxidation yielding to many intermediates is favored. Further experiments will address the intermediates formed and a more detailed study for the elucidation of the mechanism on ceria modified electrodes.

5 Conclusions

Ceria nanoparticles can be incorporated in the preparation of novel Pt/ceria composite electrodes for the electrochemical oxidation of methanol and ethanol. The oxidation current for the electrochemical oxidation in the electrodes is significantly enhanced as compared to bare Pt electrode and rivals the performance of the commercially available Pt/Ru and Pt/Ru/C bifunctional catalysts, while showing similar overpotentials for the oxidation. In the case of Pt/CeO_2 composites prepared by electrodeposition, enhanced currents over two orders of magnitude (compared to the bare Pt electrode) are observed after normalizing for surface area. Two proposed mechanisms can explain such enhancement, either by inhibiting CO adsorption or by ceria's oxygen storage capacity playing a role to ease the oxidation of adsorbed CO. The results show a great promise and a full characterization of catalytic effect of ceria on the anode's performance is further warranted.

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