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PtSnCe/C electrocatalysts for ethanol oxidation: DEFC and FTIR "*in-situ*" studies

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ABSTRACT

The ethanol oxidation reaction (EOR) was investigated using PtSnCe/C electrocatalysts in different mass ratios (72:23:5, 68:22:10 and 64:21:15) that were prepared by the polymeric precursor method. Transmission electron microscopy (TEM) showed that the particles ranged in size from approximately 2 to 5 nm. Changes in the net parameters observed for Pt suggest the incorporation of Sn and Ce into the Pt crystalline network with the formation of an alloy between Pt, Sn and/or Ce. Among the PtSnCe catalysts investigated, the 68:22:10 composition showed the highest activity toward ethanol oxidation, and the current–time curves obtained in the presence of ethanol in acidic media showed a current density 50% higher than that observed for commercial PtSn/C (E-Tek). During the experiments performed on single direct ethanol fuel cells, the power density for the PtSnCe/C 68:22:10 anode was nearly 40% higher than the one obtained using the commercial catalyst. Data from Fourier transform infrared (FTIR) spectroscopy showed that the observed behavior for ethanol oxidation may be explained in terms of a double mechanism. The presence of Sn and Ce seems to favor CO oxidation, since they produce an oxygen-containing species to oxidize acetaldehyde to acetic acid.

1. Introduction

The development of materials for ethanol oxidation reaction (EOR) is very important for improving the efficiency of direct ethanol fuel cells (DEFC) [1–5]. DEFCs are attractive devices because the fuel (ethanol) can be produced in large scale from biomass, and it is less toxic than other alcohols [6–8]. In contrast, the total oxidation of ethanol is difficult to achieve [8].

The complete electro-oxidation of ethanol to CO_2 involves 12 electrons per molecule and many adsorbed intermediates [9]. It has generally been reported that the main products formed during EOR are acetic acid and/or acetaldehyde

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[10–12]. However, ethanol is electrochemically oxidized through different pathways, and the oxidation reaction is dependent on parameters, such as the catalytic surface, the concentration of the alcohol and the pH of the environment. Thus, it is more difficult to elucidate the exact mechanism of ethanol electro-oxidation.

The high activity and stability of Pt anodes [8], especially under acidic conditions, make it a suitable electrocatalyst for the electro-oxidation of many small organic molecules. At moderate temperatures, pure platinum is not an effective anode catalyst for ethanol or methanol electro-oxidation because it is poisoned by strongly adsorbed intermediates. Adsorbed carbon monoxide (CO_{ads}) is one of the main poisoning species under these conditions. Pt-based alloys contain a second [13–15] or a third metal [6,16,17] to enhance the electrocatalytic properties of platinum by overcoming the poisoning related to methanol or ethanol electro-oxidation intermediates.

In a recent work, De Souza et al. [15] used $PtCeO_2/C$ electrocatalysts and showed that $PtCeO_2/C$ (1:3) has greater ethanol electro-oxidation activity than Pt/C and PtRu/C E-Tek materials. The higher activity was attributed to several intrinsic features, such as reduced poisoning by the strongly bound intermediates, maximum utilization of the catalyst surface for particle sizes of 4 nm and water activation by an indirect bifunctional mechanism [18–20]. Additionally Qin et al. [21] showed that the addition of CeO_2 to platinum catalysts could produce active anode catalysts for ethanol electro-oxidation. These catalysts were prepared by different procedures: 1) physically mixing the Pt/C catalyst with CeO_2, 2) adsorbing Pt nanoparticles on CeO_2 coated carbon nanotubes and 3) co-precipitating Pt(IV) ions and Ce(III) on a carbon support, followed by reduction with $NaBH_4$.

Binary materials based on Pt and Sn are reported in the literature as the most effective for ethanol oxidation [1,7,22–24]. The promoting effect of Sn on the activity of Pt catalysts has been comprehensively analyzed [1]. Based on this review and other related works [25–29], it is clear that the optimum Sn content in a binary Pt–Sn catalyst system has yet to be determined and that the optimal ratio appears to be dependent on both the cell temperature and the ratio of alloyed [22,25] and non-alloyed tin [30].

The synergic effect of ceria (used as support) and tin has been studied [31–33]. It was shown that $PtSn/CeO_2$–C electrocatalysts, prepared by an alcohol-reduction process (single step process), are more active for ethanol oxidation than the analogous PtSn/C catalysts. Fourier transform infrared (FTIR) studies of ethanol oxidation on PtSn/C electrocatalysts found that acetaldehyde and acetic acid were the main products formed, while the main products formed on $PtSn/CeO_2$–C electrocatalysts were CO_2 and acetic acid. For the product analysis, the band intensities of the species were taken into account rather than the integrated band intensities [32].

To combine the electrocatalytic effects reported for Sn alloys (electronic effect) and CeO_2 (indirect bifunctional mechanism), this work presents the preparation of PtSnCe/C electrocatalysts, using a modified polymeric precursor method (PPM) [15,22], for the ethanol oxidation reaction. The electrocatalyst was characterized by X-ray diffractometry (XRD) and transmission electron microscopy (TEM). Its performance was evaluated by chronoamperometry and polarization/density power curves in a direct ethanol fuel cell. The mechanism of EOR on PtSnCe/C electrocatalysts was studied using *in situ* FTIR spectroscopy. The results show that one of the materials synthesized (PtSnCe/C 68:22:10) combines two characteristics required for ethanol electro-oxidation: 1) a weakening of the CO-adsorption and 2) the capability to produce superficial oxides that promote the oxidation process, resulting in a material with good catalytic activity.

2. Experimental

2.1. Preparation of PtSnCe/C electrocatalysts

PtSnCe (20% w/w) on a carbon XC-72 electrocatalyst was prepared using a modified polymeric precursor method [15,22,34,35], with mass ratio of 1:50:400 (metallic precursor: citric acid (CA): ethylene glycol (EG)) was used to prepare the polymeric resin. Chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$, Sigma–Aldrich), tin chloride ($SnCl_2 \cdot 2H_2O$, Merck) and Cerium(III) chloride ($CeCl_3$, Merck) were used as precursors. After preparation, the polymeric resin was stored under refrigeration. The catalysts were prepared by placing a pre-determined volume of the resin into an appropriate amount of carbon vulcan XC-72 (Cabot Corporation), followed by the addition of sufficient EG to cover the carbon powder. The pre-determined volume of the resin was chosen to yield products containing Pt, Sn and Ce in mass ratios of 72:23:5, 68:22:10 and 64:21:15. These mixtures were homogenized in an ultrasonic bath for 60 min and thermally treated at 400 °C for 2 h in an N_2 atmosphere to remove the solvent.

2.2. Physical characterization

The XRD analysis was performed using a Rigaku Multiflex diffractometer with a CuKα radiation source. Morphological information for the catalysts was obtained with an FEI Tecnai G2 20 TEM, operating at 200 kV.

2.3. Electrocatalyst activity

Electrochemical measurements were performed at room temperature ($T = 25$ °C) with an Autolab PGSTAT 302N potentiostat. Glassy carbon (GC) was used as support for the working electrodes with 0.2 cm^2 of geometric area. A Pt sheet was used as the counter electrode, and a reversible hydrogen electrode was used as the reference. The GC support was polished to a mirror finish with 1 μm of alumina suspension and washed in a mixture of ethanol and water before each experiment. The water used in all experimental procedures was obtained from a Millipore Milli-Q system.

The working electrodes were constructed by dispersing 8 mg of the electrocatalyst powder in 1 ml water and mixing it for 5 min in an ultrasonic bath. Afterwards, 20 μl of Nafion® solution (5%) was added, and the suspension was mixed again in the ultrasonic bath for 15 min. 16 μl aliquots of the dispersion were pipetted onto the glassy carbon support surface. The electrode was dried at 60 °C for 20 min and then hydrated for 5 min in water.