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Deactivation of Palladium Electrocatalysts for Alcohols Oxidation in Basic Electrolytes

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ABSTRACT

Deactivation is one the main causes still preventing the full exploitation of palladium electrocatalysts in alkaline direct alcohol fuel cells and the electrochemical reforming of alcohols. While often attributed to the adsorption of poisoning species generated in the alcohols oxidation, in the present work we demonstrate that deactivation is provoked by the formation of palladium oxides. A combined approach including i) fuel cell runs, ii) cyclic voltammetry and iii) near edge X-ray absorption spectroscopy has enabled us to draw the conclusions reported in the paper.

1. Introduction

Nanostructured palladium has been recently employed as electrocatalyst for the catalytic oxidation of alcohols in alkaline Direct Alcohol Fuel Cells (DAFCs) [1–5] as well as in the electrochemical reforming of bioalcohols [6,7].

A combined use of palladium catalysts and alkaline electrolytes allow to completely eliminate platinum from the devices [8]. Indeed non-noble metals compounds (e.g. iron phtalocyanines) are stable in alkaline media, while they are not in acidic, and are known to effectively promote the oxygen reduction reaction [9,10]. In addition these non-noble catalysts are completely inactive toward alcohols oxidation showing no potential (and so energy efficiency) drops due to crossover through the membrane [11].

DAFCs and electrochemical reformers equipped with palladium catalysts have also been proposed as electrochemical reactors for the selective production of chemicals [2,6,7,12,13]. We have previously shown that ethanol oxidation in alkaline DAFCs results in the selective production of acetate, while e.g. the electrochemical oxidation of 1,2 propanediol on Pd lead to the formation of lactate with high selectivity [14]. Glycerol electro-oxidation has also been successfully demonstrated [13], indicating the potential of palladium electrocatalysts in the valorization of biodiesel scraps [15].

The main issue hampering the full exploitation of Pd as electrocatalyst for the electrochemical oxidation of alcohols is its lack of stability. The quest for a solution to such degradation is a subject of outstanding importance which needs for a deep understanding of its primary causes.

A few previous papers have speculated that degradation could be ascribed to the adsorption of CO, similarly to what happens in acidic environment. We believe that such CO adsorption cannot be advocated when the alcohol oxidations occurs in strong alkali. Indeed it is a consolidated fact that C–C cleavage in ethanol oxidation does not occur at pH larger than 13 on Pd catalysts [16]. Therefore we conclude that no possible pathways leading to CO adsorption occurs, or if it is so, only in a very limited, undetectable amount.

In previous papers we have hypothesized that Pd oxidation could have been the possible reason [17,18]. We formulated this

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hypothesis from indirect evidence derived by our electrochemical measurements. Particularly we have noticed that the addition of tiny amounts of sodium borohydride, a strong reducing agent, to the fuel compartment is beneficial to the DEFCs stability, supporting the role of Pd oxidation [19]. Nevertheless this doesn't completely exclude a possible role for CO adsorption.

With the present work we focus on identifying the reason for the catalyst deactivation. Through a combination of specifically designed electrochemical experiments and X-ray absorption spectroscopy we aim at proving the fundamental role of palladium oxidation to support the selection of suitable strategies for extending the life of the catalyst and ultimately devices' stability.

Among the various alcohols that can be employed in fuel cells, this investigation focuses on the use of ethanol as fuel. This choice has been operated because ethanol is selectively oxidized to acetate without C–C cleavage in strong alkali. C–C cleavage may occur on heavier alcohols instead, even at pH larger than 13 as previously observed in [20]. The lack of C_1 fragments also suggests that CO cannot be adsorbed at the electrode surface.

2. Experimental

A commercial Carbon Black (Vulcan XC-72 pellets) from Cabot Corp., USA has been employed as catalyst support. All metal salts and reagents were purchased from Aldrich and used as received. All the solutions were prepared with doubly distilled deionized water. All chemicals are of analytical grade.

Pd/C was prepared as previously described in [21]. 4.5 g of Vulcan XC-72 was suspended in 250 mL of ethylene glycol and dispersed by ultrasonication for 20 min in a 500 mL three-neck round-bottomed flask. Then an aqueous solution of H_2O (50 mL) and ethylene glycol (50 mL) and 6 mL HCl (37%) with 445 mg of dissolved $PdCl_2$ were added drop by drop to the resulting solution under stirring in a N_2 stream. After adequately stirring, an alkaline solution of NaOH (5 g) in H_2O (10 mL) and ethylene glycol (35 mL) was introduced in the reactor which then was heated at 125 °C for 3 h again under a N_2 atmosphere. Then the mixture was cool down to room temperature. The solid product was filtered off and washed with H_2O to neutral pH. The final product was dried in vacuum oven at 40 °C. An amount of 4.47 g of catalyst was obtained.

The FePc-CoPc/C cathode electro-catalyst was prepared as the method reported in [22]. Ketjen Black (5 g) was added to a mixture of iron phthalocyanine (FePc) (1.15 g) and cobalt phthalocyanine (CoPc) (1.15 g) in THF (100 mL) which was well-diversified previously by stirring for 30 min and ultrasonication for 30 min. The solvent was then removed under reduced pressure and the solid residue of FePc-CoPc/C was dried under high vacuum. After that FePc-CoPc/C was introduced into a quartz tube and heated at 600 °C under a flow of nitrogen for 2 h.

Transmission electron microscopy (TEM) was performed on a Philips CM12 microscope at an accelerating voltage of 100 kV. The microscope was equipped with an EDAX energy dispersive microanalysis system.

X-ray powder diffraction (PXRD) spectra was acquired at room temperature with a PANalytical X'PERT PRO diffractometer, employing CuKa radiation (l = 1.54187) and a PW3088/60-graded multilayer parabolic X-ray mirror for Cu radiation. The spectra was acquired in the 2q range from 5.0 to 120.08, using a continuous scan mode with an acquisition step size of 2q = 0.02638 and a counting time of 49.5 s.

Electrochemical Measurements with iR drop correction were performed with PARSTAT 2273 potentiostat/galvanostat (Princeton Applied Research) in a three electrode cell. The working electrode, Glassy Carbon (Sigradur G; 0.867 cm^2), covered by the catalyst, was loaded at the top end of the cylinder. The ink of catalyst was consisted of Pd/C (22 mg) and 2-propanol (2 g). The ink was sonicated for 2 h with a Branson 3200 bath. The metal loading on each electrode was determined by weighting the amount of ink deposited on the glassy carbon disk. An Ag/AgCl electrode was used as reference, while counter electrode was consisted of a platinum wire (0.5 mm diameter). All the solutions were purged with N_2 for at least 30 min before any electrochemical experiments.

The electrochemically active surface area (EASA) of this electrode was determined by integration of the charge in the reduction of Pd oxide region of the cyclic voltammograms (CVs) between 0.45 and 0.90 V in 2M KOH solution with the scan range of 0–1.40 V. The activation and deactivation of Pd/C was measured between the potential range of 0 and 1.2 V in 2M KOH. The activity of ethanol electro-oxidation was investigated in 2M ethanol + 2M KOH solution by cyclic voltammetry in two ranges, 0–0.75 V and 0–1.20 V. Reported CVs were acquired at a scan rate of 50 mV/s. The chronoamperometry was performed at 0.70 V for 10 h in three different electrolyte, 2M Ethanol + 2M KOH, 1 M Ethanol + 1M KOH, 0.5 M ethanol + 0.5M KOH. Chronopotentiometry test was also measured at 10 mA/cm^2 for 10 h in 2M Ethanol + 2M KOH. CVs before and after chronoamperometry or chronopotentiometry were tested to discern the deactivation of Pd/C electro-catalyst. All the potentials reported are versus to reversible hydrogen electrode (RHE).

The passive monoplanar cell test was carried out on the device composed with plexiglas as previously described [23]. The membrane-electrode assemblies (MEAs) for the passive cells were realized using a anode composed of Pd/C catalyst, a commercial Tokuyama A-006 anion-exchange membrane and a cathode containing FePc-CoPc/C electro-catalyst [22]. The membrane was conditioned in 1 M KOH solution for 1 min before assembling the MEA. The fuel loading of the anode compartment was 12 mL for each experiment. The anode catalytic ink was prepared mixing the Pd/C catalyst (100 mg) with water (400 mg) and a 5 wt% nafion solution. The resulting ink was spread onto a 5.13 cm^2 nickel foam plate to obtain a metal loading of 1 mg cm^{-2}. The MEA was obtained by mechanically pressing anode, membrane and cathode. Silicone-rubber gaskets were employed to seal the system. Power density and galvanostatic curves were determined on a ARBIN BT-2000 5A-4 channels potentiostat/galvanostat. All the experiments were performed at room temperature. New MEAs were used for each experiment and then just changed the fuel on the same MEA to test the effort of aging.

XAS data were collected at GILDA beamLine (European Synchrotron Radiation Facility, ESRF, Grenoble [24] at the palladium-K edge (24350 eV). A Si (3 1 1) double crystal monochromator was used in dynamical focusing mode; the harmonic rejection was realized by a pair of Pt mirrors, having a cutoff energy of 32 keV. Data collection was carried out in fluorescence mode using an energy resolving (energy resolution about 300 eV) 13-elements Ge fluorescence detector.

3. Results and discussion

Pd nanoparticles supported on Carbon Black exhibit the characteristic PXRD pattern of a face-centered-cubic (fcc) lattice structure as shown in Fig. 1. The strong diffraction peaks at the Bragg angles of 40.16°, 46.54°, 68.31°, 82.05° and 86.83° are respectively assigned to the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) Bragg reflections of metallic Pd. The Debye–Sherrer analysis applied to the Pd(1 1 1) reflection has returned an average particle size of 8.4 nm. Apart from the broad peak attributed to C (0 0 2) no peaks other than those of metallic Pd have been detected.

The TEM micrographs reveal the structure of our supported catalyst (Fig. 2). Particles range in between 5 and 10 nm, in good agreement with what obtained from the Debye–Sherrer analysis.