SYNTHESIS OF PtLa/C CATALYSTS FOR POLYMER ELECTROLYTE MEMBRANE FUEL CELLS

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Abstract

In the present work PtLa/C electrodes have been prepared by an alcohol reduction process to study their activity towards oxygen reduction and methanol and carbon monoxide oxidation. These electrocatalysts were compared to Pt/C in terms of activity and stability using cyclic voltammetry and steady state curves. Results show that PtLa/C materials display higher currents per gram of Pt than Pt/C for the reactions considered. In the case of methanol and CO electro-oxidation, partial removal of the adspecies from the surface takes place at more negative potentials.

Keywords: DMFC, PtLa alloys, CO oxidation, methanol oxidation, oxygen reduction.

1. Introduction

A topic of current interest for proton exchange membrane fuel cells (PEMFC) using reformed fuels and for direct methanol fuel cells (DMFC) is the search for less expensive alternative materials as electrodes. Conventionally, Pt and its alloys have been employed as electrocatalysts in these cells. However, the applicability of Pt-based electrodes is restricted because of the accumulation of surface poisoning intermediates, thus leading to loss in activity with time.

Pt sites are known to be poisoned by CO. Alloying Pt with oxophylic metals as Ru, Co, Sn or employing electronically conducting mixed oxides as electrode materials could be used to avoid the poisoning phenomenon.

A second problem in a PEMFC is the fact that the oxygen reduction reaction is slow and produces a decrease in the expected potential of the fuel cell from the theoretical 1.23_{SHE} V to $0.6\text{-}0.7_{SHE}$ V. Other limitation in the case of DMFC is the permeability of the membrane to the alcohol. The crossover of methanol to the cathode reduces the electrochemical reaction consuming O_2 to produce CO_2 and poisons the Pt with CO.

The present study applies rare earth as a co-catalyst with Pt for the cathode and anode reactions to verify whether they can reduce these limitations or not. Lanthanum is the chosen rare earth to study. Oxides and/or hydroxides of La are deposited (instead of metallic La) with metallic Pt due to fact that the reduction potential of La(III) ions is around 3.5 V [1-3] more negative than that of Pt ions. To our knowledge, in the literature there are nor systematic studies of the activity of PtLa/C catalysts towards oxygen reduction nor carbon monoxide or methanol oxidation. Thus, both the possibility to be used in the cathode and the anode of a polymer electrolyte fuel cell will be considered.

2. Experimental/Materials and Methods

2.1 Electrocatalysts preparation and characterization

PtLa/C electrodes with different Pt:La atomic ratio were prepared by an alcohol reduction process using different metal precursor concentrations and ethylene glycol as reduction agent and solvent. The electrocatalysts were prepared in alkaline environment with Vulcan XC 72 as support [4-6].

Nominal atomic ratios selected for PtLa/C were 30:70, 50:50, 60:40 and 90:10. Also a Pt/C electrode was prepared and studied. The real compositions were establish from energy dispersive X-ray (EDX) analysis (see later).

2.2 Electrochemical measurements

Conventional electrochemical measurements were carried out with a flow three electrode cell. Glassy carbon was used as counter electrode and a reference hydrogen electrode (RHE) prepared in the base electrolyte (0.5M H_2SO_4) as reference. Solutions were deoxygenated with N_2 when necessary. All experiments were performed at room temperature.

The working electrode was prepared with 40 µL of a homogeneous mixture of 4 mg of powder electrocatalyst, 1 mL of Milli-Q water and 38 µL of Nafion (Aldrich, 5%). This ink is deposited onto a glassy carbon polished surface (a disc with geometric area of 0.28 cm^2) and dried in N_2 atmosphere before its utilization.

A potentiostat/galvanostat Autolab PGSTAT30 was used for these studies. An electrochemical pretreatment by potential cycling between 0.05 and 0.40 V in the base electrolyte was applied until a stabilized cyclic voltammogram (CV) was recorded. The upper potential during cycling was maintained at 0.40 V in order to avoid La dissolution from the alloy.

A pyrolitic graphite rotating ring electrode with geometric area of 0.28 cm^2 was filled with a paste that consists in a mixture of 20 mg of electrocatalyst, 2 drops of 6% Teflon solution and Milli-Q water. A Pine Instrument Company, Analytical Rotator, Model AFASRE was used to the oxygen reduction reaction analysis.

The oxygen reduction reaction was studied with the rotating ring electrode applying a rotation speed of 2000 rpm. The steady state polarization curves were obtained starting the potential at 1.0 V, applying 0.05 V steps down to 0.30 V, and recording the current value once stabilized at the sample potential.

For CO adsorption experiments, CO was bubbled for 10 min at the adsorption potential (E_{ad} = 0.20 V). Then, the cell was washed with fresh electrolyte while bubbling N_2 during 10 min. Then, stripping of the CO adlayer was performed at 0.01 V s^{-1} from E_{ad} up to 0.85 V. Methanol electrooxidation was studied recording the CVs in a 2 M CH_3OH + 0.5 M H_2SO_4 solution for the 0.05-0.80 potential range at 0.01 V s^{-1}.

3. Results and Discussion

The composition of PtLa/C electrocatalysts was determined by EDX analysis (Table 1). It was found that the real EDX composition for all electrocatalysts was close to the nominal value.

Table 1. EDX composition of the carbon supported PtLa/C electrocatalysts

Nominal composition	Pt	La
PtLa 30:70	37	63
PtLa 50:50	57	43
PtLa 60:40	68	32
PtLa 30:70	93	7

Results for the reduction of O_2 at the different PtLa/C catalysts from rotating disk measurements are given in Figure 1. It is shown that PtLa/C materials display higher currents per gram of Pt than Pt/C, raising the reduction current values as the content of

La is increased. Thus, that best catalysts for oxygen reduction appears to be that with the composition Pt:La 30:70.

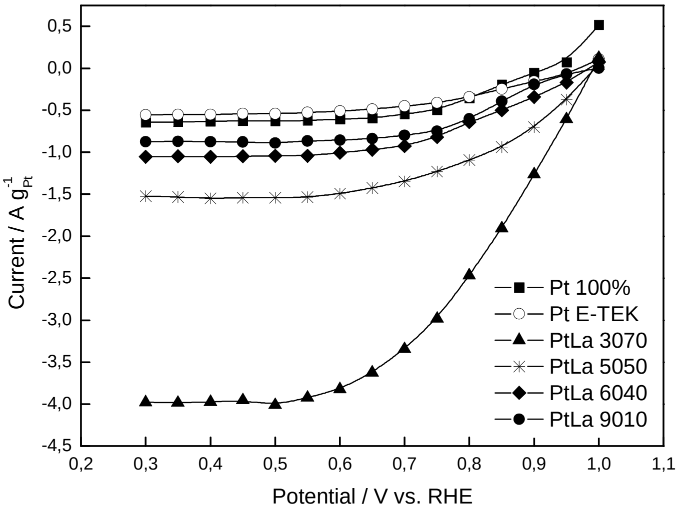

Figure 1. Steady state polarization curves for oxygen reduction at PtLa/C prepared with different atomic composition in 0.5 M H_2SO_4 at 2000 rpm.

Adsorption and oxidation of carbon monoxide has been performed for all PtLa/C catalyst. Figure 2 shows the stripping at 0.01 Vs^{-1} of the adsorbate formed at 0.20 V for PtLa/C with an atomic composition 1:1. It is observed that the onset for CO oxidation occurs at 0.48 V attaining a peak at 0.80 V with a shoulder at 0.70 V. The main difference with respect to Pt/C is the appearance of this shoulder and the shift to more negative potentials of the beginning of the oxidation current, which indicates that partial removal of the adspecies from the surface can take place at these catalysts at lower potentials. Thus, this contribution seems to be related to the presence of La oxides/hydroxides.

CVs for the electro-oxidation of methanol using the Pt:La compositions of 30:70, 50:50, 60:40 and 90:10 as working electrodes are given in Figure 3. In this case also the best results were obtained for PtLa/C with the composition 30:70: this catalyst presents the onset at more negative potentials (0.47 V) and the highest mass current values from all compositions studied.

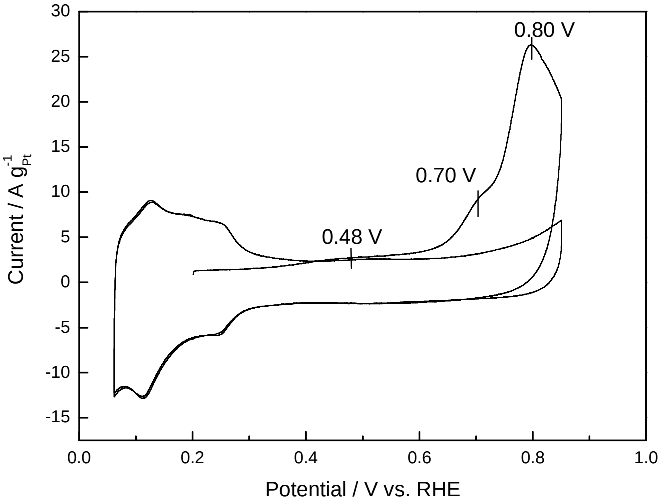

Figure 2. CV for CO stripping of PtLa/C 1:1 at 0.01 mVs^{-1} in 0.5M H_2SO_4.

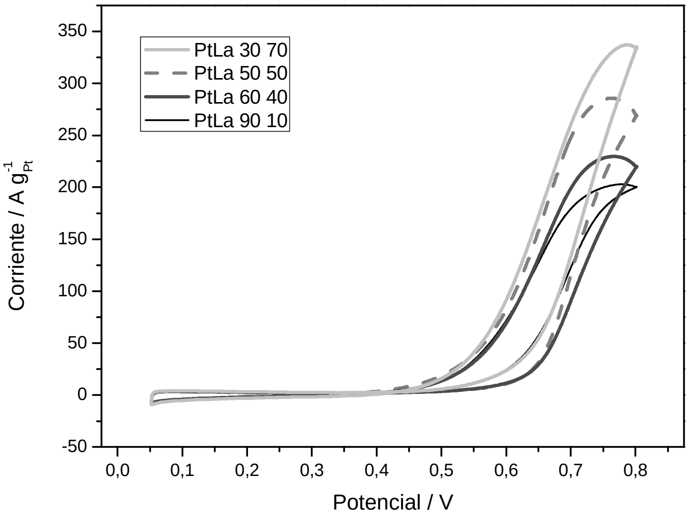

Figure 3. CVs for PtLa/C with compositions 30:70, 50:50, 60:40 and 90:10 recorded at 0.01 mVs^{-1} in 2 M CH_3OH + 0.5 M H_2SO_4.

These features allow concluding that lanthanum oxide/hydroxides are helping in the oxidation of methanol by increasing the overall rate accordingly to the La content.

Probably it is due to the removing of CO from poisoning Pt during the oxidation process.

5. Conclusions

In the present paper, electronically conducting mixed lanthanum oxides/hydroxides with Pt supported on carbon, have been used as electrode materials to reduce the poisoning effects of reformed fuels for PEMFC and in methanol oxidation for DMFC. Cyclic voltammetry and polarization curves show that the presence of La in the catalysts has an influence in the electrocatalytic behavior of the electrodes. Thus, it is established an enhancement of the current values for oxygen reduction as the content of lanthanum is increased. Similar results are observed for methanol oxidation applying cyclic voltammetry. Finally, from CO stripping studies it is shown that there is a shift to more negative potentials of the onset removal potential of CO_{ad} from the surface due to the presence of lanthanum oxides/hydroxides.

Acknowledgements

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