

Characterization of Proton Exchange Membrane Fuel Cell Cathode Catalysts Prepared by Alcohol-Reduction Process

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Keywords: PEMFC, Rare earth, Hydrogen, Electrocatalysis

Abstract. Pt/rare-earth cathode catalysts were synthesized by the alcohol-reduction process and its structure was investigated by transmission electron microscopy (TEM), energy dispersive analyses (EDS), X-ray Diffraction (XRD). The electrochemical behavior of the cathode catalyst was analyzed by cyclic voltammetry (CV) and chronoamperometry (CA).

Introduction

Significant progress was made during the last years regarding the commercialisation of fuel cells. However, one major challenge still remaining is the large overvoltage of the oxygen reduction reaction (ORR) at the cathode, leading to a significant loss of efficiency of the fuel cell system [1]. The electrocatalyst dispersed on a carbon support is tailored to induce four-electron reduction of oxygen to water by utilizing the protons that permeate from the anode compartment. Although the anode compartment provides optimum performance, the improvement in the cathode compartment is being sought continuously [2]. The shift in the ORR electrocatalysis has been ascribed to different factors such as changes in the Pt–Pt interatomic distance [3,4], the surface area [3,5] and, particularly, the Pt electronic configuration [3,6]. Therefore, it is not surprising that basic as well as applied research aims at the development of oxygen reduction catalysts.

Most of this previous work has focused on examining electrocatalysts containing elements which by themselves are stable in electrochemical systems and determining whether or not these electrocatalysts are active toward the reaction of interest limiting the search space for new electrocatalyst compositions to elements in or near the platinum metal group. Recently, however, it has expanded the search space for new electrocatalyst compositions to regions outside of the platinum metal group. Molybdenum and tin, have been incorporated into platinum-based electrocatalysts [7].

This paper takes a complementary approach to that mentioned above. The chosen element to be investigated was lanthanum that can easily form stable oxides as a rare earth does. It may be a strong oxidizing agents helping the ORR at the cathode.

The aim of this paper is to present the results of ORR at Pt-lanthanum oxide/C electrodes that have shown an enhanced rate constant for this reaction.

Experimental

There were prepared Pt/C and different PtLa/C atomic ratio electrodes by an alcohol reduction process using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Aldrich) and $\text{LaCl}_3 \cdot x\text{H}_2\text{O}$ (Aldrich) as metal sources,

ethylene glycol (Merck) as solvent and reducing agent [8,9]. The electrocatalysts were prepared in alkaline environment with Vulcan XC 72 as support [9,10]. Dispersive X-ray (EDX) analysis using a scanning electron microscope Philips XL30 with a 20 keV electron beam and provided with EDAX DX-4 microanalyser was used to establish their nominal composition.

The oxygen reduction electrochemical studies of the electrocatalysts were carried out using the thin porous coating technique [10]. An amount of 20 mg of the electrocatalyst was added to a solution of 50 mL of water containing 3 drops of a 6% polytetrafluoroethylene (PTFE) suspension. The resulting mixture was treated in an ultrasound bath, filtered and transferred to the cavity.

In chronoamperometry experiments the currents values (I) were expressed in amperes and were normalized ($A_{g_{Pt}}^{-1}$) per gram of platinum. The quantity of platinum was calculated considering the mass of the electrocatalyst present in the working electrode multiplied by its percentage of platinum. For these experiments, the working electrode was a pyrolytic graphite rotating ring with a PTFE cylinder with a cavity 0.15 mm deep and 0.28 cm² area. The reference electrode was a reference hydrogen electrode (RHE) and the counter electrode was a platinized Pt plate. Electrochemical measurements were made using a Pine Instrument Company, Analytical Rotator, Model AFASRE applying a rotation speed of 2000 rpm and a potentiostat/galvanostat Autolab PGSTAT30. The steady state polarization curves were obtained starting the potential at 1.0 V, applying 0.05 V steps down to 0.30 V in the base electrolyte (H₂SO₄ 0.5 mol L⁻¹), and recording the current value once stabilized at the sample potential.

XRD analyses were performed using a Rigaku diffractometer model Multiflex with a CuK α radiation sources. 2 θ angles form 10° to 90° and recorded at a scanning speed of 2° min⁻¹.

Transmission electron microscopy (TEM) was carried out using a JEOL JEM-2100 (200 kV) [11,12,13].

The particle size distributions were determined by measuring the nanoparticles from micrographs using Image Pro Plus 6.

Results and discussion

Different atomic ratio of PtLa/C and Pt/C electrocatalysts (20 wt%) were prepared in a single step using ethylene glycol as solvent and reducing agent in presence of carbon Vulcan XC72R [8,9]. As the reduction potential of La is about 3.5 V negative of that for Pt [7], it is not possible to reduce La(III) ions in the conditions used in the chosen methodology. Thus, the electrocatalysts were prepared in alkaline medium in order to deposit La(III) ions as lanthanum oxide or hydroxide and Pt(IV) ions, which were reduced by ethylene glycol, as metallic Pt on the carbon support.

To evaluate whether or not the electrocatalysts chemical composition was effective, EDX analysis were carried out. Table 1 presents the obtained atomic ratio.

Table 1. PtLa/C (90:10), (60:40), (50:50) and Pt/C electrocatalysts atomic ratio

| Electrocatalysts | Atomic Ratio |
|------------------|--------------|
| Pt:La 90:10 | 93:07 |
| Pt:La 60:40 | 68:32 |
| Pt:La 50:50 | 57:43 |

EDX evaluation of the PtLa/C catalysts composition show that the atomic ratios of Pt:La are approximately the same of the nominal ratios. It was done the same analysis with a blank containing a well known nominal ratio and the results were similar to the synthesized electrocatalysts. This results show that Pt and La oxides/hydroxides were successfully loaded to the carbon support without obvious loss.

To provide crystallite structure information of the catalysts as well as average particle size, X-ray diffraction analysis was carried out.

Different X-ray diffractograms of the Pt/C and PtLa/C electrocatalysts are shown in Figure 1. In all diffractograms a broad peak at about 25° was associated with the Vulcan XC72R support material, due to the (002) phase of the hexagonal structure of this carbon [14]. The diffractogram of Pt/C and PtLa/C electrocatalyst showed peaks at approximately $2\theta = 40^\circ$, 47° , 67° and 82° , which are associated with the (111), (200), (220) and (311) planes, respectively, of the fcc structure characteristic of platinum [14]. The diffractogram of PtLa/C electrocatalyst with Pt:La atomic ratio of 50:50 and 60:40 showed the peaks characteristic of fcc Pt, the presence of peaks of La_2O_3 26° , 29° , 34° , 56° (JPDF 000-83-1354) and the presence of peaks of $\text{La}(\text{OH})_3$, 27° , 31° , 43° (JPDF 000-75-1900). [15]

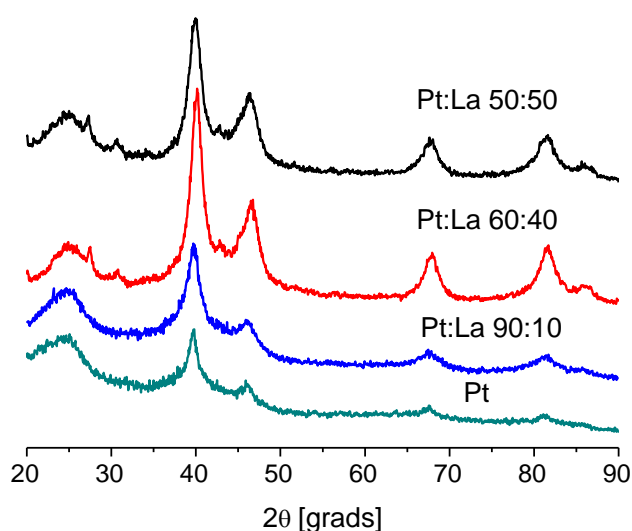


Fig. 1. X-ray diffraction patterns of the PtLa/C (90:10), (60:40), (50:50) and Pt/C electrocatalysts.

The reflections of Pt(220) were used to calculate the average particle size according to the Scherrer formula [14]. The average particle size of PtLa/C (90:10), (60:40), (50:50) and Pt/C are shown in Table 2. It can be observed a variation of 3.0 to 5.5 nm, what indicates that the alcohol reduction method was quite efficient in the synthesis of the electrocatalysts.

Table 2, Average particle size of PtLa/C (90:10), (60:40), (50:50) and Pt/C electrocatalysts obtained from the Pt(220) plane using Sherrer formula.

| Electrocatalysts | Average Particle Size [nm] |
|------------------|----------------------------|
| Pt:La 90:10 | 5.0 |
| Pt:La 60:40 | 5.5 |
| Pt:La 50:50 | 5.5 |
| Pt | 3.0 |

The distribution of the particles on the carbon support was analysed through TEM images and the average particle size of PtLa/C (90:10), (60:40), (50:50) and Pt/C electrocatalysts obtained from Image Pró Plus 6.

Figure 2 shows the typical TEM image of the Pt/C catalyst. As can be seen from this figure, the platinum particles in the Pt/C catalyst are uniform and well distributed. Based on the measurements of 100 particles in random regions (Table 3), the average particle size is estimated to be 2.0 nm for the Pt/C catalyst. While for the PtLa/C catalyst, the nanoparticles on carbon are uniform in most regions but coalescent in others, with an average particle size of approximately 4.9 nm. It can be observed in Table 3 that the values of the average particle size obtained by TEM analysis are almost in agreement with those calculated from the XRD results.

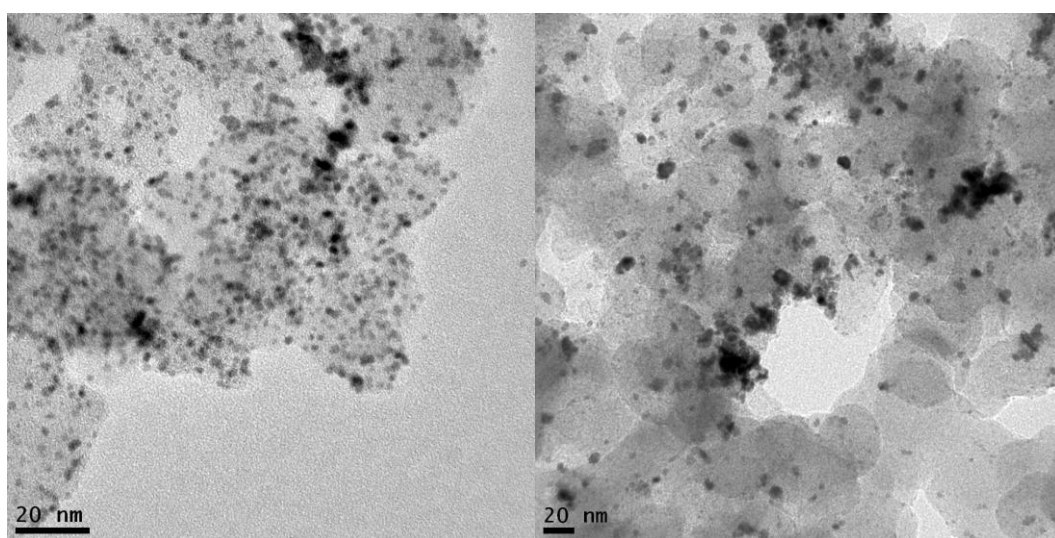


Figure 2. TEM image Pt/C and PtLa/C (50:50) electrocatalysts.

Table 3. Average particle size of PtLa/C (90:10), (60:40), (50:50) and Pt/C electrocatalysts obtained from TEM micrograph through Image Pró Plus 6.

| Electrocatalysts | Average Particle Size (TEM) |
|------------------|-----------------------------|
| Pt:La 90:10 | 4.523 ± 0.084 |
| Pt:La 60:40 | 5.215 ± 0.175 |
| Pt:La 50:50 | 4.888 ± 0.196 |
| Pt | 1.917 ± 0.032 |

The electrochemical behavior of the cathode catalyst was analyzed by chronoamperometry for the oxygen reduction on PtLa/C (50:50), PtLa/C (60:40), PtLa/C (90:10), Pt/C and commercial Pt/C E-TEK. Figure 3 presents the steady state polarization curves obtained in O₂ saturated 0.5 mol L⁻¹ H₂SO₄ solution and 2000 rpm rotating rate. The starting potential was 1V and it was applied 0.05V steps down to 0.3V obtaining the current limit into 2 minutes.

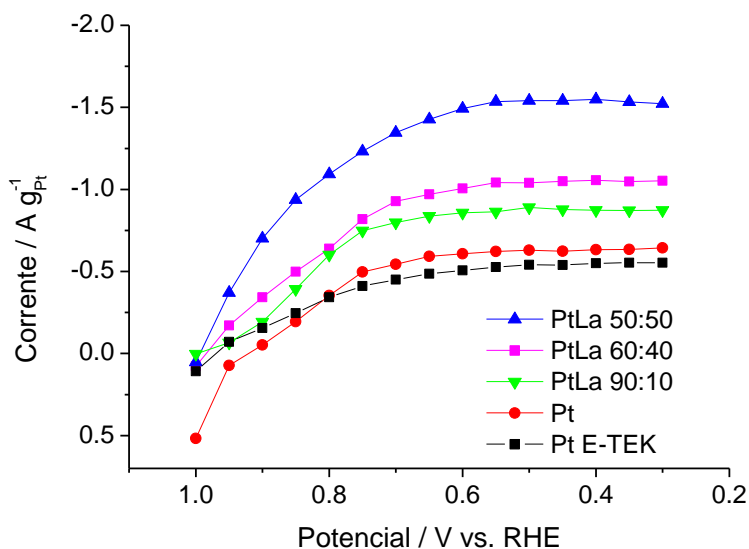


Figure 3. Steady state polarization curves for oxygen reduction at PtLa/C with different atomic ratios in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution at 2000 rpm.

Electrochemical measurements, in Figure 3, revealed that the addition of these oxides significantly improves the electrode performance for oxygen reduction, in terms of the reaction activity. Higher currents are obtained with the implementation of the La atomic ratio in the electrocatalyst.

Conclusion

The addition of La(III) oxide/hydroxide into Pt catalysts can significantly improve the electrode performance for oxygen reduction, in terms of the reaction activity. Alcohol-reduction process in alkaline medium could produce active PtLa/C electrocatalysts. The X-ray diffractogram of PtLa/C electrocatalysts showed the typical fcc structure of platinum and the presence of La(III) oxides and hydroxides. TEM images of the Pt/C catalyst showed that the particles in the Pt/C catalyst are uniform and well distributed. PtLa/C catalyst, the nanoparticles on carbon are uniform in most regions but with some agglomerate regions. The average particle size obtained by TEM analysis is almost in good agreement with those calculated from the XRD results. PtLa/C (50:50), PtLa/C (60:40), PtLa/C (90:10) electrocatalysts presented higher current values than Pt/C and this current increased with the implementation of La in the atomic ratio.

Acknowledgement

The authors thank CNPq, CAPES and FAPESP for financial support.

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