Synthesis of Unsupported Pt-Based Electrocatalysts and Evaluation of their Catalytic Activity for the Ethylene Glycol Oxidation Reaction

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ABSTRACT

Pt, Pt-Ru, Pt-CeO_2 and Pt-Ru-CeO_2 electrocatalysts were synthesized and evaluated as anodes for the ethylene glycol oxidation reaction (EGOR). The nanomaterials were prepared by slowly dropping the precursors in a $NaBH_4$ solution, in a reduction process of 10 min. The results from the electrochemical characterization of the anodes, carried out in 0.5 M H_2SO_4, showed that the Pt-Ru material possess a higher catalytic activity for the EGOR, compared to Pt-alone, Pt-CeO_2 and (Pt-Ru)-CeO_2. The nano-sized Pt-Ru anode demonstrated a high stability in accelerated potential cycling tests, with very low surface losses in the hydrogen adsorption/desorption region after 500 cycles.

1.-Introduction

Nanostructured materials present many interesting properties as catalysts for electrochemical devices such as Direct Alcohol Fuel Cells (DAFCs). This has been the reason why many researchers have generated a large interest in their study. However, although many systems are investigated, nowadays is necessary to study different Pt-based materials with specific catalytic properties for the type of fuel being used in DAFCs. Catalysts like Pt-Ru, Pt-CeO_2 or Pt-Ru- CeO_2 are of interest for DAFCs because of their high performance. The main objective of this research is to evaluate the performance of metallic nano-particles for the ethylene glycol oxidation reaction.

Cerium-modified Pt materials have shown good electrochemical behavior as anodes for DAFCS. Research has been carried out on structure, chemical properties, reduction behavior, stoichiometry, storage capacity and metal-cerium interactions [1-8]. It is also important to determine which of the materials with a Ce percentage may find application as environmental catalysts [4,6,9-15]. The presence of Ce in the crystalline structure has a positive effect, for example enhancing the storage and release of oxygen. This is crucial in several catalytic reactions such as the Oxygen Reduction Reaction (ORR) and the oxidation of organic molecules in fuel cells.

The metallic nano-particles Pt, Pt-Ru, Pt-CeO_2, Pt-Ru-CeO_2 were synthesized with sodium borohydride ($NaBH_4$). The materials were evaluated as anodes for the oxidation of $C_2H_6O_2$, via cyclic voltammetry (CV) and lineal scan voltammetry (LSV). The physicochemical characterization included EDAX and your crystal structures XRD.

2.-Experimental

The reagents used to obtain nanoparticles were $RuCl_3$ (Aldrich, 45.55% Ru), $H_2PtCl_6*6H_2O$ (Aldrich, 37.5% Pt base), and $CeN_3O_9*6H_2O$ (Aldrich, 99%), as metallic sources and $NaBH_4$ (Aldrich, solución 12% p/v in NaOH 14 M), as reducing agent. All reagents were used without further treatment. The synthesis was performed by slowly dropping the precursors in a $NaBH_4$ solution, in a reduction process of 10 min. The recovered powders were washed with excess water and dried in a furnace at eighty degrees. Figure 1 shows, a schematic diagram of the experimental procedure during the synthesis of nanoparticles. The molar ratio used for obtaining the powders is shown in Table 1.

The catalytic activity of the Pt-based materials for the EGOR was evaluated with the aid of a potentiostat (Voltalab) connected to a RDE instrument (Pine Inst.). CVs and LSVs were obtained in N_2-saturated 0.5 M H_2SO_4. The methods used to prepare catalytic inks and working electrodes has already been described with detail elsewhere [16].

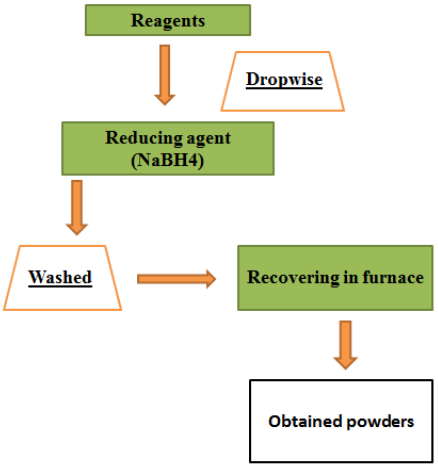

Figure 1. Schematic diagram showing the synthesis procedure of the nanomaterials.

Table 1.- Reagents molar ratio

Metallic materials	Reagents			Reducing agent
Salts precursor	$H_2PtCl_6*6H_2O$	$RuCl_3$	CeN3O9*6H2O	$NaBH_4$
Pt	0.000513 M			0.000075 M
Pt-Ru	0.001538 M	0.002950 M		0.001299 M
Pt-CeO2	0.001538 M		0.002141 M	0.000599 M
Pt-Ru-CeO2	0.001026 M	0.001967 M	0.001427 M	0.001115 M

3.-Results and discussion

Figure 2 shows the voltamperograms the four catalysts synthesized in this work. The CV of Pt depicts the typical characteristics of this metal. The CV of Pt-CeO_2 also shows a Pt-like shape. Meanwhile, the Pt-Ru and Pt-Ru-CeO2 anodes show less defined H_{ads} regions, probably due to the formation of a Pt-Ru alloy phase.

Figure 3 depicts the LSVs of the EGOR at the anodes studied here. The four catalysts demonstrate a degree of catalytic activity for this reaction. However, evaluating the peak current density in the positive going potential scan, it can be observed that the Pt-Ru anode delivers a higher current density (peak maximum of ca. 7 mA/cm^2) compared to the other three catalysts. This material also shows a less intense peak current density peak in the negative-going scan, indicating that smaller amounts of EG and/or intermediates remain at the catalytic surface, i.e., the oxidation of the molecule is more efficient at Pt-Ru. The catalytic activity for the EGOR decreases in the order Pt-Ru>Pt>Pt-CeO_2>Pt-Ru-CeO_2. Currently, we are investigating the catalysts by TEM to clarify their morphological characteristics and make a correlation with the catalytic activity toward the EGOR.

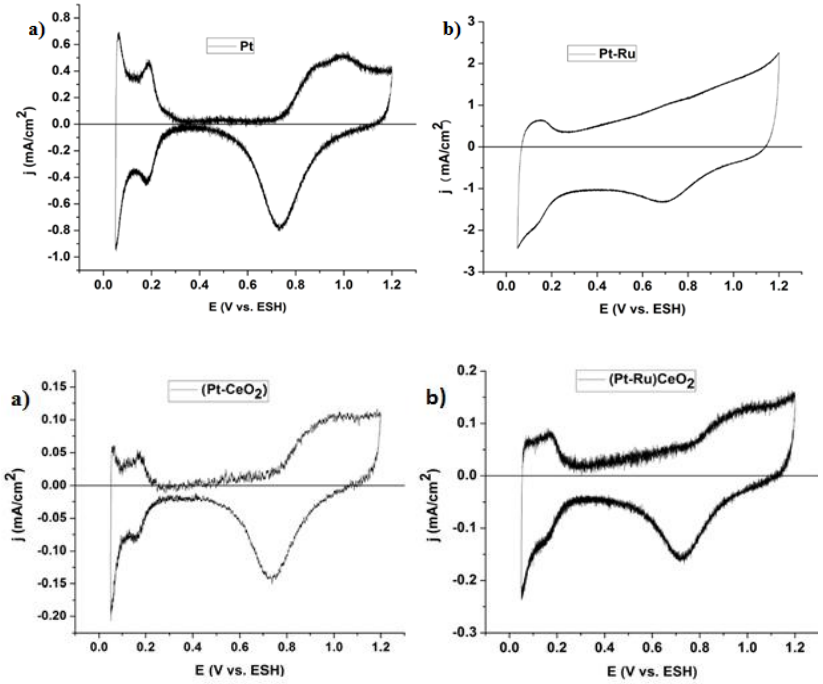

Figure 2.- CVs of Pt, Pt-Ru, Pt-CeO_2 and Pt-Ru-CeO_2. Scan rate 20mV/s.

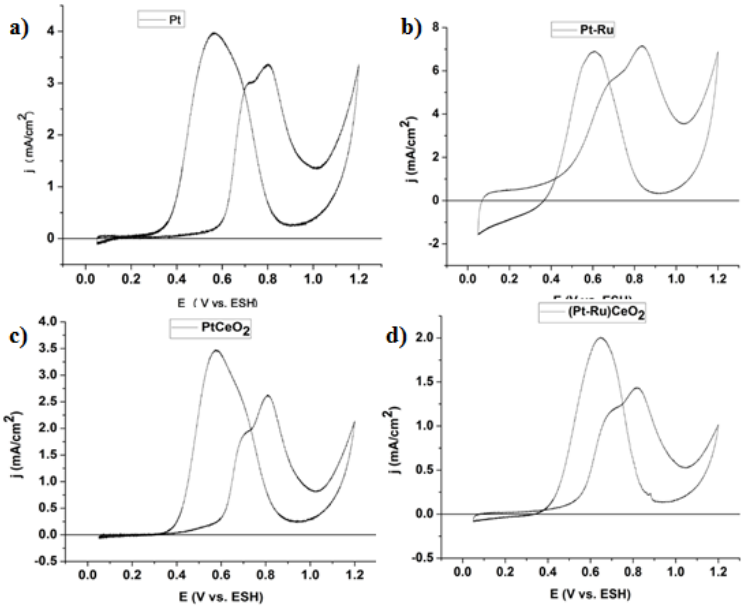

Figure 3. LSVs of the EGOR at Pt, Pt-Ru, Pt-CeO_2 and Pt-Ru-CeO_2. Scan rate 20mV/s.

4.-Conclusions

We synthesized and evaluated nanostructured catalysts for the EGOR. In acid medium, the catalytic activity of the anodes decreases in the order: Pt-Ru>Pt>Pt-CeO_2>Pt-Ru-CeO_2. Currently, we are investigating the catalysts by TEM to clarify their morphological characteristics and make a correlation with the catalytic activity toward the EGOR.

5.-Akcnowledgements

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