Electrochemical Behavior of Pd-based Nanocatalysts (Hollow@Me@Pd/C) for Direct Alcohol Oxidation in Alkaline Medium

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The synthesis and application of *core@shell* nanocatalyst with high morphological organization became an attractive research area in fuel cells due to the large increase in the organic molecules oxidation, promoted by these nanostructured catalytic surfaces.

Several palladium-based electrocatalysts have been used as anode in Direct Alcohol Fuel Cell (DAFCs). However, some difficulties such as high cost concerning noble metal loading, low power obtained by the single cell tests, reduced efficiency of C-C bond breaking for a total fuel oxidation, and problems with catalyst poisoning have limited the technology application for large-scale systems. Although the application of this electrocatalysts class have been increasing, the behavior and performance for the alternative fuels oxidation such as ethanol, ethylene glycol, and glycerol are not completely understood.

The electrochemical characterization of the Pd-based catalyst (Hollow@Me@Pd/C), applied to electro-oxidation of ethanol, ethylene glycol, and glycerol in alkaline medium is reported.

The catalysts were prepared by co-reduction of their metallic precursors (Me^{n+}_{core} – $PdCl_4^{2-}{}_{shell}$, 40 wt% metal loading on carbon XC-72R, in a atomic ratio of Pd:Me = 1:1) by the $NaBH_4$ added dropwise. To promote electrostatically self-assembled was employed sodium dodecylsulfate (SDS) in order to maintain strucuture-directing agent. The SDS surfactant forms micelles in aqueous solution, with the apolar tail facing the center and the polar heads ($–OSO^{3-}$) composing the outer layer, weakly negatively charged.

The crystalline structure and composition of prepared catalysts were characterized using X-ray Diffraction (XRD) and Energy Dispersive X-ray Analysis (EDX). The electrochemical behaviour and the catalytic activity of the prepared catalysts towards the alcohols oxidation were measured by means of cyclic voltammetry and chronoamperometry.

Table 1 shows the lattice parameters, volume and crystallite size of the catalysts synthesized.

Table 1. XRD pattern parameters of *Hollow@Me@Pt/C* electrocatalysts.

Composition	Phase	a (Å)	b (Å)	c (Å)	V (Å)	D (200) / nm
$Ni_{32}@Pd_{68}/C$	Pd	3.89022	-----	-----	58.9057	2.26
$Ru_{25}@Pd_{75}/C$	Pd	3.89652	-----	-----	59.1602	2.00
$Sn_{52}@Pd_{48}/C$	Pd	3.90430	-----	-----	59.5147	4.16
	SnO_2	4.76290	-----	3.1785	72.1061	-----

Catalysts presented characteristic (111), (200) and (222) Pd diffraction peaks (JCPDS PDF 00-046-1043) with small shifts in 2θ, indicating the absence of alloys formation. For the Sn@Pd/C composition was observed peaks related to SnO_2 phase. The calculated mean sizes according to the diffraction peak of Pd (200) are found to be in the range of 4.2 to 2.0 nm.

Figure 1 displays the representative cyclic voltammetric curves for the different catalyst compositions.

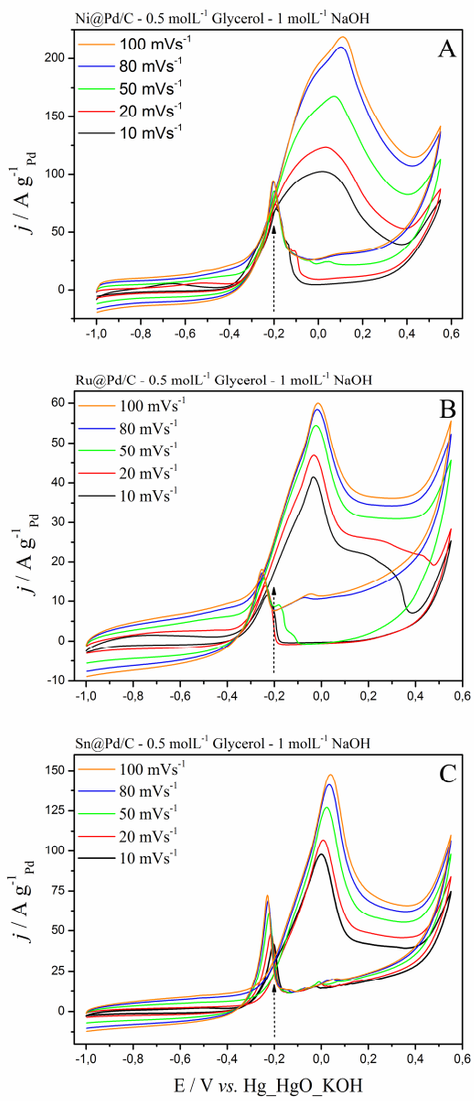

Figure 1. Representative cyclic voltammograms of Ni@Pd/C (A), Ru@Pd/C (B), and Sn@Pd/C (C) in 0.5 $molL^{-1}$ Glycerol + 1.0 $molL^{-1}$ NaOH at different potential sweep rates.

The results showed good response of these nanocatalyst compositions for the fuels oxidation. Chronoamperometry results indicate the following order of fuels reactivity: Ethanol < Glycerol < Ethylene Glycol.

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References

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