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Niobium as co-electrocatalyst for Pd in Alkaline Medium: Improved Selectivity and Mechanism for Ethanol Electrooxidation Reaction

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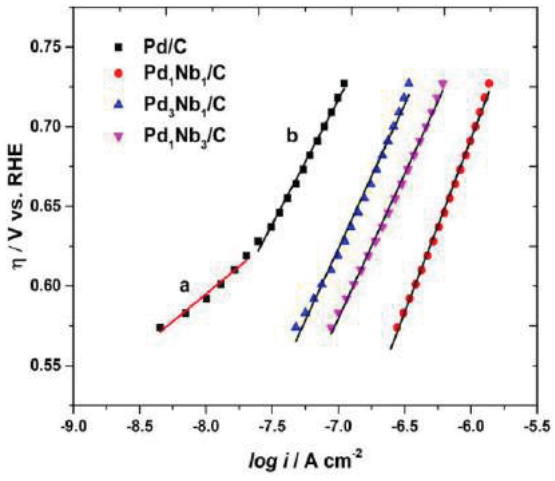
Highlights

Pd/C with Nb nanoparticles shows highest current exchange density in Tafel plots. FTIR *ex situ* spectra indicated that Pd_1Nb_1/C displayed the minimum production of acetaldehyde.

Resumo/Abstract

Direct ethanol fuel cells (DEFC) have been evaluated as a possible alternative source of sustainable energy, because it can reach high current densities with minimal pollutant production [1]. In this work, we report the synthesis of Pd_xNb_y/C binary electrocatalysts supported on Vulcan XC-72 carbon by the sol-gel method [2]. These synthesized electrocatalysts were physically characterized by DRX, EDS, ICP-MS, XPS and TEM. Their electrochemical activities (CV and CA) were evaluated as already reported by Souza [2]. Here, we reported new results from Tafel plots and FTIR *ex situ* experiments for ethanol oxidation reaction using those electrocatalysts.

Figure 1. Tafel plot of EOR from LSV using 1.0 mol L^{-1} ethanol and 1.0 mol L^{-1} KOH, at 1 mV s^{-1} and room temperature.



Pd/C electrocatalyst has the EOR governed by two determining steps since it showed two straight lines between 570 mV and 730mV, presenting also two different slopes (a and b, in Figure 1). Unlike the other electrocatalysts, with Nb in their chemical composition, that the EOR occurs by one determining step since there is just one slope. The exchange current densities (A cm^{-2}) were $2.3x10^{-17}$, $2.7x10^{-12}$, $6.6x10^{-10}$, $3.6x10^{-11}$ and $7.3x10^{-11}$ for Pd/C[a], Pd/C[b], Pd_1Nb_1/C, Pd_3Nb_1/C and Pd_1Nb_3/C, respectively. This shows that Nb increases the electron exchange rate at the analyte/electrode interface, improving the kinetics of the EOR reaction [3]. FTIR experiments strengthened the evidence that Nb modifies the Pd mechanism for EOR electrocatalysis to a mechanism that present almost no formation of acetaldehyde, avoiding the reaction $CH_3CH_2OH_{ads} + 2\,OH^-_{ads} \rightarrow CH_3CHO_{ads} + 2\,H_2O_{ads} + 2e^-$. The FTIR spectra showed that Pd_1Nb_1/C displays the highest production of CO_2 and the lowest production of acetaldehyde. Furthermore, the ADT experiments with ICP-MS analysis indicated that Pd_1Nb_1/C obtained the highest peak current density during 1000 cycles of the experiment, presenting the lowest Pd mass loss after the ADT.

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